

CA  
1  
EP  
53079  
E02

Environment  
Canada

Environnement  
Canada

DRAFT  
UNEDITED

Environmental  
Protection  
Service

Service de la  
protection de  
l'environnement

CA 1 EP53079E02



# NATIONAL INVENTORY OF NATURAL SOURCES AND EMISSIONS OF SULPHUR COMPOUNDS

Earth Sciences Library

To be published at a later date as:  
Economic and Technical Review  
Report EPS 3-AP-79-2

Air Pollution Control Directorate  
May 1979



Digitized by the Internet Archive  
in 2025 with funding from  
University of Toronto

<https://archive.org/details/31761056865611>

DRAFT  
UNEDITED

This report was prepared for the Pollution Data Analysis Division, Air Pollution Control Directorate, Environment Canada, by The Environmental Applications Group Limited of Toronto, Ontario. The report is being released to the scientific community prior to review, editing and formal publication by Environment Canada in order to disseminate the scientific information contained therein as quickly as possible. Release does not signify that the contents necessarily reflect the views and policies of Environment Canada.

The Environmental Applications Group Limited  
Toronto, Ontario



Prepared for  
Pollution Data Analysis Division  
Air Pollution Control Directorate  
Environmental Protection Branch  
Environment Canada

May 1979

Department of Supply and Services  
Ottawa, P.Q. K1A 0S5







# TABLE OF CONTENTS

DRAFT  
UNEDITED

## NATIONAL INVENTORY OF NATURAL SOURCES AND EMISSIONS OF SULPHUR COMPOUNDS

### GLOSSARY

|    |         |     |
|----|---------|-----|
| 1. | SUMMARY | 1-2 |
|----|---------|-----|

|    |                                    |     |
|----|------------------------------------|-----|
| 2. | SULPHUR BUDGETS FOR THE ATMOSPHERE | 2-1 |
|----|------------------------------------|-----|

|     |              |     |
|-----|--------------|-----|
| 2.1 | INTRODUCTION | 2-1 |
|-----|--------------|-----|

|     |                             |     |
|-----|-----------------------------|-----|
| 2.2 | COMPARATIVE SULPHUR BUDGETS | 2-1 |
|-----|-----------------------------|-----|

|     |                            |     |
|-----|----------------------------|-----|
| 2.3 | ATMOSPHERIC CONCENTRATIONS | 2-2 |
|-----|----------------------------|-----|

|     |                                                 |      |
|-----|-------------------------------------------------|------|
| 2.4 | PAIRS OF SULPHUR COMPOUNDS IN THE<br>ATMOSPHERE | 2-11 |
|-----|-------------------------------------------------|------|

|    |                                                                        |     |
|----|------------------------------------------------------------------------|-----|
| 3. | GENERATION MECHANISMS AND FLUX RATES<br>OF NATURAL ATMOSPHERIC SULPHUR | 3-1 |
|----|------------------------------------------------------------------------|-----|

|     |                  |     |
|-----|------------------|-----|
| 3.1 | BIOGENIC SOURCES | 3-1 |
|-----|------------------|-----|

|       |                       |     |
|-------|-----------------------|-----|
| 3.1.1 | Terrestrial Processes | 3-1 |
|-------|-----------------------|-----|

|       |                   |     |
|-------|-------------------|-----|
| 3.1.2 | Aquatic Processes | 3-7 |
|-------|-------------------|-----|

|     |                       |      |
|-----|-----------------------|------|
| 3.2 | OTHER NATURAL SOURCES | 3-11 |
|-----|-----------------------|------|

|       |       |      |
|-------|-------|------|
| 3.2.1 | Spray | 3-11 |
|-------|-------|------|

|       |                        |      |
|-------|------------------------|------|
| 3.2.2 | Canals and Hot Springs | 3-11 |
|-------|------------------------|------|

|       |            |      |
|-------|------------|------|
| 3.2.3 | Soils Dust | 3-11 |
|-------|------------|------|

|       |              |      |
|-------|--------------|------|
| 3.2.4 | Forest Fires | 3-11 |
|-------|--------------|------|

|    |                                                   |     |
|----|---------------------------------------------------|-----|
| 4. | SULPHUR EMISSION RATES AND PRODUCTIVITY<br>MARINE | 4-1 |
|----|---------------------------------------------------|-----|

|     |                             |     |
|-----|-----------------------------|-----|
| 4.1 | SULPHUR PRODUCTIVITY MARINE | 4-1 |
|-----|-----------------------------|-----|

|     |                  |     |
|-----|------------------|-----|
| 4.2 | BIOGENIC SOURCES | 4-1 |
|-----|------------------|-----|

|       |            |     |
|-------|------------|-----|
| 4.2.1 | Vegetation | 4-1 |
|-------|------------|-----|

|       |         |     |
|-------|---------|-----|
| 4.2.2 | Aquatic | 4-1 |
|-------|---------|-----|

by

The Environmental Applications Group Limited  
Toronto, Ontario

prepared for

Pollution Data Analysis Division  
Air Pollution Control Directorate  
Environmental Protection Service  
Environment Canada

May 1979

Department of Supply and Services  
Contract No. 04SS-KE204-1080



# TABLE OF CONTENTS

|                                                                           | <u>Page No.</u> |
|---------------------------------------------------------------------------|-----------------|
| GLOSSARY                                                                  | i               |
| 1. SUMMARY                                                                | 1-1             |
| 2. SULPHUR BUDGETS FOR THE ATMOSPHERE                                     | 2-1             |
| 2.1 INTRODUCTION                                                          | 2-1             |
| 2.2 COMPARATIVE SULPHUR BUDGETS                                           | 2-3             |
| 2.3 ATMOSPHERIC CONCENTRATIONS                                            | 2-7             |
| 2.4 FATE OF SULPHUR COMPOUNDS IN THE<br>ATMOSPHERE                        | 2-11            |
| 3. GENERATION MECHANISMS AND FLUX RATES<br>OF NATURAL ATMOSPHERIC SULPHUR | 3-1             |
| 3.1 BIOGENIC SOURCES                                                      | 3-1             |
| 3.1.1 Terrestrial Processes                                               | 3-1             |
| 3.1.2 Aquatic Processes                                                   | 3-7             |
| 3.2 OTHER NATURAL SOURCES                                                 | 3-11            |
| 3.2.1 Sea Spray                                                           | 3-11            |
| 3.2.2 Volcanoes and Hotsprings                                            | 3-17            |
| 3.2.3 Soils Dust                                                          | 3-20            |
| 3.2.4 Forest Fires                                                        | 3-22            |
| 4. SULPHUR EMISSION RATES AND PRODUCTIVITY<br>RANKING                     | 4-1             |
| 4.1 SULPHUR PRODUCTIVITY RANKING                                          | 4-1             |
| 4.2 BIOGENIC SOURCES                                                      | 4-3             |
| 4.2.1 Soils                                                               | 4-3             |
| 4.2.2 Vegetation                                                          | 4-7             |
| 4.2.3 Aquatic                                                             | 4-10            |



|       |                                             |      |
|-------|---------------------------------------------|------|
| 4.3   | OTHER NATURAL SOURCES                       | 4-13 |
| 4.3.1 | Sea and Lake Spray                          | 4-13 |
| 4.3.2 | Soil Dust                                   | 4-16 |
| 4.3.3 | Forest Fires                                | 4-17 |
| 4.3.4 | Miscellaneous                               | 4-19 |
| 5.    | ANNUAL NATURAL SULPHUR EMISSIONS FOR CANADA | 5-1  |
| 5.1   | BIOGENIC SOURCES                            | 5-1  |
| 5.1.1 | Soils                                       | 5-9  |
| 5.1.2 | Vegetation                                  | 5-39 |
| 5.1.3 | Aquatic                                     | 5-42 |
| 5.2   | OTHER NATURAL EMISSIONS                     | 5-46 |
| 6.    | DATA GAPS AND UNCERTAINTIES                 | 6-1  |
| 7.    | REFERENCES                                  | 7-1  |

# TABLES

|     |                                                                  | Page No. |
|-----|------------------------------------------------------------------|----------|
| 1-1 | SUMMARY OF CANADIAN NATURAL SULPHUR EMISSIONS                    | 1-3      |
| 2-1 | GLOBAL SULPHUR BUDGETS                                           | 2-4      |
| 2-2 | BACKGROUND CONCENTRATIONS OF SULPHUR COMPOUNDS                   | 2-8      |
| 2-3 | RESIDENCE TIMES                                                  | 2-12     |
| 3-1 | PERCENT CONTRIBUTION OF SEA-SALT SULPHATE IN WET DEPOSITION      | 3-12     |
| 3-2 | SEA-SALT SULPHATE CONCENTRATIONS IN AIR                          | 3-14     |
| 3-3 | SEA-SALT SULPHATE PRODUCTION AS A FUNCTION OF WINDSPEED          | 3-16     |
| 4-1 | SULPHUR PRODUCTIVITY RANKING                                     | 4-1      |
| 4-2 | SOIL CLASSIFICATIONS AND SULPHUR PRODUCTIVITY RANKINGS           | 4-4      |
| 4-3 | PRODUCTION OF VOLATILE SULPHUR FROM CANADIAN SOILS               | 4-6      |
| 4-4 | DMS EMISSION RATES FROM VEGETATION                               | 4-7      |
| 4-5 | MARINE BIOGENIC CLASSIFICATIONS AND SULPHUR PRODUCTIVITY RANKING | 4-12     |
| 4-6 | SEA-SALT EMISSION RATES FOR COASTAL AREAS                        | 4-14     |
| 4-7 | ANNUAL SULPHUR EMISSIONS FROM FOREST FIRES                       | 4-17     |
| 4-8 | SULPHUR EMISSIONS FROM FOREST FIRES IN ONTARIO, 1971-1976        | 4-18     |
| 5-1 | ANNUAL EMISSIONS OF SULPHUR FROM SOILS -Provincial Summary       | 5-10     |
| 5-2 | COUNTY RANKING AND SULPHUR PRODUCTION                            | 5-11     |
|     | Newfoundland                                                     | 5-11     |
|     | Nova Scotia                                                      | 5-12     |
|     | Prince Edward Island                                             | 5-13     |
|     | New Brunswick                                                    | 5-14     |

|                       |      |
|-----------------------|------|
| Québec                | 5-16 |
| Ontario               | 5-22 |
| Manitoba              | 5-27 |
| Saskatchewan          | 5-29 |
| Alberta               | 5-31 |
| British Columbia      | 5-33 |
| Northwest Territories | 5-37 |
| Yukon Territory       | 5-38 |

|     |                                                                |      |
|-----|----------------------------------------------------------------|------|
| 5-3 | VEGETATION EMISSIONS                                           | 5-40 |
| 5-4 | SULPHUR PRODUCTION BY VEGETATION                               | 5-41 |
| 5-5 | SULPHUR EMISSION RANKING FOR COASTAL SHORELINE<br>HABITATS     | 5-43 |
| 5-6 | CANADIAN COASTAL SULPHUR EMISSIONS                             | 5-44 |
| 5-7 | ESTIMATED BIOGENIC SULPHUR PRODUCTION FROM<br>FRESHWATER LAKES | 5-45 |
| 5-8 | SULPHUR FROM SEA-SALT SPRAY                                    | 5-47 |
| 5-9 | LAKE SULPHATE EMISSIONS                                        | 5-48 |



## FIGURES

Page No.

|     |                                                      |     |
|-----|------------------------------------------------------|-----|
| 1.  | INDEX MAP                                            | 5-2 |
| 2.  | CENSUS DIVISION DISTRIBUTION - MARITIME PROVINCES    | 5-3 |
| 3.  | CENSUS DIVISION DISTRIBUTION - QUEBEC                | 5-4 |
| 4.  | CENSUS DIVISION DISTRIBUTION - ONTARIO               | 5-5 |
| 5.  | CENSUS DIVISION DISTRIBUTION - PRAIRIE PROVINCES     | 5-6 |
| 6.  | CENSUS DIVISION DISTRIBUTION - BRITISH COLUMBIA      | 5-7 |
| 7.  | CENSUS DIVISION DISTRIBUTION - TERRITORIES           | 5-8 |
| 8.  | SOIL AND MARINE CLASSIFICATIONS - MARITIME PROVINCES |     |
| 9.  | SOIL AND MARINE CLASSIFICATIONS - QUEBEC             |     |
| 10. | SOIL AND MARINE CLASSIFICATIONS - ONTARIO            |     |
| 11. | SOIL AND MARINE CLASSIFICATIONS - PRAIRIE PROVINCES  |     |
| 12. | SOIL AND MARINE CLASSIFICATIONS - BRITISH COLUMBIA   |     |
| 13. | SOIL AND MARINE CLASSIFICATIONS - TERRITORIES        |     |

Note: Figures 8-13 are at the back of the report.

## GLOSSARY

### Units

|                              |                                                                                                                                                         |
|------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------|
| Mass:                        | ug = microgram = $10^{-6}$ grams<br>mg = milligram = $10^{-3}$ grams<br>MT = metric ton = $10^6$ grams<br>Tg = teragram = $10^{12}$ grams               |
| Area:                        | ha = hectare = $10^4$ square metres<br>= $10^{-2}$ square kilometres                                                                                    |
| Concentration:               | ugS m <sup>-3</sup> = micrograms (of a sulphur compound) as sulphur per cubic metre                                                                     |
| Transfer and Emission Rates: | gS hr <sup>-1</sup> = grams (of a sulphur compound) as sulphur per hour<br>TgS yr <sup>-1</sup> = teragrams (of a sulphur compound) as sulphur per year |

Note: all concentrations and emission rates are based on sulphur unless otherwise specified, for example:

$$\begin{aligned}1 \text{ ug SO}_2 \text{ m}^{-3} &= 0.5 \text{ ugSm}^{-3} \\1 \text{ ug H}_2\text{S m}^{-3} &= 0.94 \text{ ugSm}^{-3}\end{aligned}$$

### Chemical Nomenclature

|                  |                     |
|------------------|---------------------|
| COS              | carbonyl sulphide   |
| CS <sub>2</sub>  | carbon disulphide   |
| DMS              | dimethyl sulphide   |
| DMDS             | dimethyl disulphide |
| H <sub>2</sub> S | hydrogen sulphide   |
| MeSH             | methyl mercaptan    |
| S                | elemental sulphur   |
| SO <sub>2</sub>  | sulphur dioxide     |
| SO <sub>4</sub>  | sulphate            |



## 1. SUMMARY

A principal objective of the Long-Range Transport of Air Pollutants Program within the Department of the Environment is the development of the capability to realistically assess and predict air quality and pollution emissions in North America. Emission inventories for Canada and the U.S.A. are required to use production models and assess the impact of loadings.

An important aspect of the emission of sulphur compounds is the contribution from natural sources. These sources include water bodies, marshes, volcanic activity, the decay of plant matter, and other biological processes.

While the existence of natural sulphur contributions to the atmosphere has been recognized for at least 35 years (Conway 1942), interest in the magnitude of these emissions has been heightened by recent evidence that biogenic sulphur sources may make significant contributions to the atmospheric load of particulate sulphate which can be transported over large distances.

This study presents a nationwide inventory of natural emissions of sulphur compounds to the atmosphere and an evaluation of their contribution to the overall sulphur burden of ambient air. A literature search and review was undertaken to obtain available data on estimates of natural emissions of sulphur compounds. Data in this field are relatively sparse and in some cases contradictory which makes some reported estimates of source emissions quite speculative. These emission rates are



considered to be preliminary and subject to revision. The overall total natural emissions of sulphur presented herein are likely to be only accurate to within an order of magnitude.

The major natural sulphur compound emitted by biological processes to the atmosphere is hydrogen sulphide. In addition, other compounds have been detected, including carbon disulphide, carbonyl sulphide, dimethyl sulphide, and methyl mercaptan. Forest fires produce sulphur dioxide while sulphates are released into the atmosphere from sea and lake sprays.

The total Canadian sulphur emission from natural sources was estimated to be approximately 500,000 metric tons per annum. The total industrial sulphur emissions are about 3,000,000 metric tons. The most productive regions for natural sulphur releases occur on the Atlantic and Pacific coasts and in the provinces of Ontario and Quebec.

Table 1-1 provides a regional breakdown of sulphur emissions in Canada by source category. Each of these sources and its contribution to the Canadian atmosphere is summarized in the following discussion.

TABLE 1-1

SUMMARY OF CANADIAN NATURAL, SULPHUR EMISSIONS  
(metric tons S per year)

|                        | BIOGENIC EMISSIONS |        |        |            | OTHER NATURAL SOURCES    |                      |           |       | FOREST FIRES |
|------------------------|--------------------|--------|--------|------------|--------------------------|----------------------|-----------|-------|--------------|
|                        | SOILS              | MARINE | LAKES  | VEGETATION | SEA SALT SO <sub>4</sub> | LAKE SO <sub>4</sub> | SOIL DUST |       |              |
| Newfoundland           | 1,561              | 35,500 | 203    | 139        | 101,200                  | 120                  |           | 81    |              |
| New Brunswick          | 740                |        | 100    | 278        |                          | 5                    |           |       |              |
| Prince Edward Is.      | 72                 |        | -      | 200        |                          |                      |           |       |              |
| Nova Scotia            | 606                |        | 102    | 226        |                          | 3                    |           |       |              |
| Quebec                 | 23,400             |        | 1,471  | 1,772      |                          | 60                   |           |       |              |
| Ontario                | 65,944             | 4,375  | 3,543  | 2,698      |                          | 3,020                |           | 55    |              |
| Manitoba               | 47,860             |        | 2,650  | 552        |                          | 1,090                |           | 203   |              |
| Saskatchewan           | 16,373             |        | 2,434  | 1,245      |                          | 260                  |           | 164   |              |
| Alberta                | 31,830             |        | 654    | 1,016      |                          | 40                   |           | 64    |              |
| British Columbia       | 27,976             | 10,470 | 810    | 795        |                          | 27,300               |           | 50    | 171          |
| Yukon                  | 4,950              | 84     |        |            | 60,400                   | 1,340                |           | 194   |              |
| North West Territories | 22,770             |        |        |            |                          |                      |           |       |              |
| CANADA                 | 244,082            | 50,429 | 11,898 | 8,918      | 188,900                  | 7,190                | 500       | 1,000 |              |

CANADA'S TOTAL - 512,917



## Soils

Losses of sulphur to the atmosphere from soils occur as a result of two main processes: microbial anaerobic reduction of sulphate and bacterial methylation. The former mechanism produces large amounts of hydrogen sulphide particularly under high moisture conditions. The second process evolves methylated organic compounds such as dimethyl sulphide and dimethyl disulphide. The sulphur emissions for Canada were estimated from flux rates cited in the literature and applied to soils types in Canada on a census division basis. The annual total emissions of sulphur compounds from this source is 244,758 metric tons.

## Aquatic

Hydrogen sulphide is emitted in coastal areas and freshwater lakes by two mechanisms. The first relates to decomposition of organically-bound sulphur, and the second results from the reduction of inorganic sulphate under anaerobic conditions. Sulphate reduction to sulphide has been suggested as the pre-dominant process in aquatic systems. Emission rates of  $H_2S$  vary considerably with highest  $H_2S$  releases occurring in highly productive estuarine ecosystems, swamps and marsh areas. The emissions from this source were estimated using measured flux rates applied to various coastal divisions and lake categories of Canada. The total sulphur emission estimated from this source is about 60,000 metric tons per annum.

## Vegetation

Leaves of trees and herbs produce dimethyl sulphide but the actual production mechanism is not known. During senescence, leading to the death of leaves on the whole plant, sulphur release rates have been shown to increase



10 - 100 times. The annual sulphur production from vegetation decreases northward and is related to shorter growing seasons and lower summer temperatures. The total release from this source is estimated to be 8,900 metric tons per annum.

#### Sea and Lake Spray

Water droplets from sea and lake surfaces are released to the atmosphere by the action of waves, creating myriads of bursting bubbles. These water droplets, which subsequently evaporate, contain sulphate along with other chemical constituents prevalent in sea and lake water. A wind-dependent emission rate for this source was derived and applied to the coastal areas of Canada. An estimated 189,000 metric tons (as sulphur) of sea salt sulphate are released to the atmosphere annually. Similarly, it is estimated that Canadian freshwater lakes release about 7,000 metric tons of sulphur per year.

#### Soils Dust

Wind entrainment of dust particles which contain sulphur, contributes to the atmospheric sulphur burden. Only sparse data are available on production rates of soil dust and sulphur content of arid soils. The main areas prone to wind erosion are located in Alberta and Saskatchewan, with a few small areas in British Columbia. An annual sulphur emission of 500 metric tons was estimated for this source.

#### Forest Fires

Sulphur dioxide has been detected during forest fires. Based on estimated flux rates and the average area of forests destroyed by fire in Canada, the annual sulphur release is estimated to be 1,000 metric tons.





## 2. SULPHUR BUDGETS FOR THE ATMOSPHERE

### 2.1 INTRODUCTION

Global budgets provide a means of determining the fluxes and burdens in the sulphur cycle without having to investigate the details of each individual process (i.e. the generation mechanism of reduced sulphur compounds released to the atmosphere from soils). They help in identifying the most significant uncertainties about the circulation of compounds. However, global sulphur budgets have the weakness that they form an average over extremely diverse conditions in different parts of the world. In the following sections the atmospheric reservoir is examined along with those reservoirs which are sources to the atmosphere. As well, an attempt is made to determine which reduced sulphur compounds are prevalent in the atmosphere.

The global sulphur cycle involves four reservoirs - atmosphere, hydrosphere, lithosphere, and biosphere - and transfers between these reservoirs. Conway (1942) first determined that the world's rocks contain too little sulphur, by a factor of three, to account for the sulphate delivered by rivers to the ocean. This deficiency implied that three quarters of the total sulphur loading of the oceans originated from the atmosphere. Of this amount, about one third, or a quarter of the total budget, was assumed to originate from industrial sources.

To account for the remaining two thirds, or half the total budget, Conway hypothesized a production of hydrogen sulphide ( $H_2S$ ) over the shelf areas of the ocean which reached the atmosphere. This atmospheric sulphur was carried in over the continents and contributed to the river run-off of sulphur to the ocean, balancing the global sulphur budget. However, despite this hypothesis, Eriksson (1959) noted that it was not certain whether cycled sulphur reached the land as a sea spray particle or as a reduced sulphur compound such as  $H_2S$ . Using isotope techniques, Jensen (1962) resolved the problem in favour of reduced sulphur compounds. Lighter isotopes of sulphur appear preferentially in reduced compounds such as  $H_2S$ . Even if a gaseous reduced compound is oxidized in the atmosphere, the sulphur remains isotopically light. Jensen found that atmospheric sulphate over the oceans contained a smaller proportion of heavy sulphur isotopes than did sulphate in seawater. From this result he concluded that a component of the atmospheric sulphate over the ocean did not originate from sea spray but must be formed from reduced sulphur compounds.



## 2.2 COMPARATIVE SULPHUR BUDGETS

There have been various attempts to develop global atmospheric sulphur budgets to determine the relative importance of sulphur sources. These budgets have yielded estimated rates for the release of sulphur to the atmosphere from anthropogenic, sea spray, biogenic and volcanic sources. Table 2-1 lists the sulphur fluxes of the aforementioned sources into the air from data provided by various authors.

Although each estimated source flux in the budget has large fluctuations in relative contribution, the greatest controversy centers on the contribution of biogenic sources which produce the reduced compounds necessary to balance the budget. Granat (1976) used a production rate of  $5 \text{ TgSyr}^{-1}$  of dimethyl sulphide (estimated by Hitchcock 1975) from land and marine sources and added  $27 \text{ TgSyr}^{-1}$  of other natural sulphur compounds to balance his budget.

The estimates of biogenic emissions have decreased over the years (see Table 2-1). This trend is supported somewhat by experimental observations. Nriagu and Coker's (1978) isotope composition measurements of sulphur in precipitation indicate that biogenic release of sulphur may be considerably smaller than figures employed in most budgets. Jaesckhe et al (1978), interpreted their  $\text{H}_2\text{S}$  flux rate results as being unable to support present global biogenic estimates. Hitchcock (1975), using Lovelock et al (1972) measured flux rates, estimated that DMS emissions to the atmosphere only contribute about 2 to  $5 \text{ TgSyr}^{-1}$ .

TABLE 2-1

## GLOBAL SULPHUR BUDGETS

(TgSyr<sup>-1</sup>)

| Source                    | Eriksson<br>(1963) | Junge<br>(1963) | Robinson &<br>Robbins<br>(1970) | Kellogg<br>et al<br>(1972) | Friend<br>(1973) | Granat<br>(1976) |
|---------------------------|--------------------|-----------------|---------------------------------|----------------------------|------------------|------------------|
| Pollution                 | 40                 | 40              | 70                              | 50                         | 65               | 65               |
| Biological decay          |                    |                 |                                 |                            |                  |                  |
| Land                      | 110                | 70              | 68                              | 90                         | 58               | 32               |
| Marine                    | 170                | 160             | 30                              |                            | 48               |                  |
| Sea Spray                 | 40                 | *               | 44                              | 43                         | 44               | 44               |
| Volcanic                  | -                  | -               | -                               | 1.5                        | 2                | 3                |
| Soil Dust                 | -                  | -               | -                               | -                          | -                | 0.2              |
| Total Atmospheric<br>Flux | 365                | 315             | 212                             | 184.5                      | 217              | 144.2            |

\* Junge's model was for excess sulphur only so sea salt component was not included



Several important observations and conclusions can be made from the present status of global atmospheric budgets:

1. Biogenic estimates vary with changes in contribution from anthropogenic sea spray and volcanic sources due to back-calculation techniques.
2. In recent years, emission estimates from biogenic sources have generally decreased in magnitude.
3. Hydrogen sulphide and dimethyl sulphide do not appear to account for the majority of biogenic emissions; other reduced organic sulphur compounds may be required to balance the atmospheric sulphur budget.
4. The relative contributions from land and sea biogenic sources vary greatly.

Recently, the re-examination of sulphur budgets has noted inconsistencies which indicate that the biogenic sources may be as large as originally estimated by Junge (1963) and Eriksson (1963). Nothunson (1979) noted errors in the budget by Robinson and Robbins (1970) which caused them to underestimate the contribution from biogenic sources by  $44 \text{ TgSyr}^{-1}$ . This increases their biological decay component from  $118 \text{ TgSyr}^{-1}$  to  $162 \text{ TgSyr}^{-1}$ .

Hitchcock (1978) re-estimated natural sulphur releases from the ocean on the basis of total sulphate in river discharge, corrected for rock weathering, anthropogenic releases, and volcanic and hydrothermal sources. The figures she obtained indicate an annual sulphur release of about 200 to 250  $\text{TgSyr}^{-1}$  (including sea salt) from the oceans which agrees with the estimates of early workers in the field (cf Eriksson, Junge in Table 2-1).

Although the values provided in Table 2-1 must be regarded as rough estimates, in some cases within an order of magnitude, the flux of a reduced form of sulphur from biological decay processes cannot be eliminated. Because these budget estimates are so uncertain they are of little use in determining the strength of natural emissions in Canada. However, an attempt was made by Katz (1977) to derive a sulphur budget for Canada on the basis of the Kellogg et al (1972) global budget. Katz estimated that biogenic sources and sea salt would release 5.02 and 1.7 TgSyr<sup>-1</sup> to the Canadian atmosphere, respectively.



### 2.3 ATMOSPHERIC CONCENTRATIONS

Representative background concentrations for reduced sulphur compounds, carbonyl sulphide, sulphur dioxide, and particulate sulphate are given in Table 2-2. Data are still sparse for hydrogen sulphide and organic sulphur compounds because no techniques were available until recently to provide reliable sampling and detection at the very low levels existing in the atmosphere.

The background concentrations of  $\text{H}_2\text{S}$  over land are generally larger than those reported over marine areas supporting the hypothesis that land surfaces contribute more hydrogen sulphide to the sulphur budget. Meszaros (1978), reviewing atmospheric concentration data, assumed an average  $\text{H}_2\text{S}$  global concentration of  $0.14 \text{ ugSm}^{-3}$ .

Only two measurements of carbonyl sulphide ( $\text{COS}$ ) concentrations have been made and they range in value from 0.27 to  $0.67 \text{ ugSm}^{-3}$  (Hanst et al. 1975, Sandalls and Penkett, 1977). Sandalls and Penkett (1977) observed an average concentration of  $0.42 \text{ ugSm}^{-3}$  for carbon disulphide ( $\text{CS}_2$ ). No measurements of background concentrations of methyl mercaptan have been made, but Sandalls and Penkett (1978) suggest a concentration of  $0.005 \text{ ugSm}^{-3}$  based upon Cox's (1975) estimated residence time of 0.09 days (see Section 2.4). Maroulis and Bandy (1976) measured levels of about  $0.07 \text{ ugSm}^{-3}$  for dimethyl sulphide (DMS) off the Atlantic Coast of the United States.

The data on concentrations of sulphate and sulphur dioxide (to a lesser extent) are provided to illustrate possible levels maintained by hydrogen sulphide or other natural gaseous sulphur compounds.

## BACKGROUND CONCENTRATIONS OF SULPHUR COMPOUNDS

(ugS/m<sup>3</sup>)

| Terrestrial                                                                        | Marine                                                                                              | Assumed Global Average                                                                                                |
|------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|
| Hydrogen Sulphide (H <sub>2</sub> S)                                               |                                                                                                     |                                                                                                                       |
| 0.13-0.4 Wales<br>Smith <u>et al.</u> (1961)                                       | 0.01 Barbados, Sal.Is.<br>Slatt <u>et al.</u> (1978)                                                | 0.26 Robinson &<br>Robbins (1968)                                                                                     |
| 0-0.4 Panama<br>Axelrod <u>et al.</u> (1969)                                       | 0.06 Southern Florida<br>Slatt <u>et al.</u> (1978)                                                 | 0.23 Friend (1973)                                                                                                    |
| 0.03 - 0.09 Colorado<br>Natusch <u>et al.</u> (1972)                               | 0.09 North Sea<br>Georgii (1978)                                                                    | 0.14 Meszaros (1978)                                                                                                  |
| 0.10-0.26 Illinois &<br>Missouri<br>Breeding <u>et al.</u> (1973)                  | 0.09 North Sea<br>Jaeschke (1977)                                                                   |                                                                                                                       |
| 0.09 Rhine-Main<br>Georgii (1978)                                                  |                                                                                                     |                                                                                                                       |
| Carbonyl Sulphide (COS)                                                            |                                                                                                     |                                                                                                                       |
| 0.27 North Caroline<br>Hanst <u>et al.</u> (1975)                                  |                                                                                                     |                                                                                                                       |
| 0.67 England<br>Sandalls &<br>Penkett (1977)                                       |                                                                                                     |                                                                                                                       |
| Carbon Disulphide (CS <sub>2</sub> )                                               |                                                                                                     |                                                                                                                       |
| 0.42 England<br>Sandalls &<br>Penkett (1977)                                       |                                                                                                     |                                                                                                                       |
| Methyl Mercaptan (CH <sub>3</sub> SH)                                              |                                                                                                     |                                                                                                                       |
|                                                                                    |                                                                                                     | 0.005 Sandalls &<br>Penkett (1977)<br>(from residence time<br>to contribute 70 TgS<br>yr <sup>-1</sup> to atmosphere) |
| Dimethyl Sulphide (DMS)                                                            |                                                                                                     |                                                                                                                       |
|                                                                                    | 0.07-0.08 Atlantic<br>Maroulis & Bandy<br>(1976)                                                    |                                                                                                                       |
| Sulphur Dioxide (SO <sub>2</sub> )                                                 |                                                                                                     |                                                                                                                       |
| 0.5-1.7 Caribbean<br>0.4-1.4 Panama<br>0.4 Brazil<br>Lodge <u>et al.</u><br>(1974) | 0.09 N. Atlantic<br>Prahm <u>et al.</u> (1975)<br>0.05 S. Pacific<br>Nguyen <u>et al.</u><br>(1974) | 0.5 Ocean<br>Georgii (1978)<br>up to 1.7 Land<br>Granat (1976)                                                        |
| 0.25 Germany<br>Georgii (1978)                                                     | nil 0-5°N Atlantic<br>0.25 Atlantic<br>Georgii (1978)                                               |                                                                                                                       |



TABLE 2-2 (Cont'd)

| Terrestrial                        |                  | Marine                                                       |                            | Assumed Global Average |                         |
|------------------------------------|------------------|--------------------------------------------------------------|----------------------------|------------------------|-------------------------|
| Sulphur dioxide (SO <sub>2</sub> ) |                  |                                                              |                            |                        |                         |
|                                    |                  | 0.3 -1.5 (probably contains anthro-pogenic SO <sub>2</sub> ) |                            | 30-60°N Atlantic       |                         |
|                                    |                  | Meszaros (1978)                                              |                            |                        |                         |
| Excess sulphate (SO <sub>4</sub> ) |                  |                                                              |                            |                        |                         |
| <0.3                               | Canada           | 0.1-0.5                                                      | Atlantic                   | 1-2                    | N. Hemisphere           |
|                                    | Chung (1978)     |                                                              | Gravenhorst (1978)         |                        | Castleman <u>et al.</u> |
| 0.17                               | Non Urban area   | 0.04-0.1                                                     | Pacific                    |                        | (1974)                  |
| 1-3                                | Rural N. America |                                                              | Gillette & Blifford        | 0.6                    | S. Hemisphere           |
|                                    | Meszaros (1978)  |                                                              | (1971)                     |                        | Granat (1976)           |
|                                    |                  | 0.14                                                         | N. Atlantic                | 0.1-0.5                | Land                    |
|                                    |                  |                                                              | Prahm <u>et al.</u> (1975) |                        | Granat (1976)           |
|                                    |                  | 0.3*                                                         | S. Pacific                 | 0.1-0.5                | Ocean                   |
|                                    |                  | 0.006*                                                       | Indian Ocean               |                        | Granat (1976)           |
|                                    |                  |                                                              | Meszaros & Vissy           |                        |                         |
|                                    |                  |                                                              | (1974)                     |                        |                         |

\* uncertain estimate based on particle size # frequency distributions

The precursor of a portion of the background sulphur dioxide is likely to be natural sulphur gases (see Section 2.4). However, the relative contribution of natural gaseous compounds to sulphur dioxide levels cannot be inferred directly from concentrations given in Table 2-2. The short and variable residence times of gaseous sulphur precludes the attainment of a steady state condition. The existence of lower  $\text{SO}_2$  concentrations over the oceans, compared to those observed over land, might indicate a decreased production of precursor gases in these regions. However, seawater is an  $\text{SO}_2$  sink (Liss and Slater 1974) which might account entirely for the reduced  $\text{SO}_2$  levels over the oceans.

Investigations by Gravenhorst (1976) into the composition of sulphate particles in unpolluted air over the ocean have shown that sulphate concentration of aerosols in marine air is always in excess compared with the sulphate content of oceanwater. The contribution of non-maritime sulphate to total atmospheric sulphate over the ocean was 60-80 percent. Reported levels of excess sulphate have ranged from less than  $0.006 \text{ ugSm}^{-3}$  over the Indian Ocean (Meszaros and Vissy 1974) to  $3 \text{ ugSm}^{-3}$  over rural land areas (Meszaros 1978).

Excess sulphate may have gaseous precursors such as DMS emanating from the ocean. If this is the case, the measurements of Meszaros and Vissy (1974) support a higher production of reduced sulphur compounds in warm waters near the equator. Unlike sulphur dioxide, there is no discernible difference between  $\text{SO}_4$  concentrations over continents and over oceans.



## 2.4 FATE OF SULPHUR COMPOUNDS IN THE ATMOSPHERE

The compounds of sulphur in the atmosphere from natural sources may include hydrogen sulphide, sulphur dioxide, dimethyl sulphide, dimethyl disulphide, and methyl mercaptan. The generally accepted hypothesis is that reduced sulphur compounds introduced into the atmosphere are oxidized to sulphates with sulphur dioxide as a possible intermediate. The residence times and removal mechanisms of various compounds are given in Table 2-3.

The rate of production or atmospheric residence time of natural sulphur compounds is most commonly estimated by application of a steady state model in which rates of production and removal are equal. Assuming that the removal process is a first order kinetic process, the atmospheric residence time is given by

$$\tau = \frac{Cs}{R} \cdot M \quad (1)$$

where  $\tau$  = atmospheric residence time

Cs = average concentration of sulphur compound

R = rate of production

M = mass of the atmosphere

Junge (1963), Friend (1973), Kellogg et al. (1973) and Slatt et al. (1978) have used this relationship to estimate the atmospheric lifetime of  $H_2S$  (see Table 2-3). However, Slatt et al. (1978) have pointed out limitations in using this approach. First of all, the assumption of a steady state concentration is tenuous. Even if the average concentration of  $H_2S$  in the atmosphere may be constant, this concentration does not represent a steady state in terms of chemical kinetics.

TABLE 2-3

## RESIDENCE TIMES

| Reference                            | Residence Time          | Remarks                                                                                                                                                    |
|--------------------------------------|-------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Hydrogen Sulphide (H <sub>2</sub> S) |                         |                                                                                                                                                            |
| Cox (1975)                           | 2.3 days                | reaction with OH radicals                                                                                                                                  |
| Jorgensen (1977)                     | 1-5 days                |                                                                                                                                                            |
| Kellogg <u>et al.</u><br>(1973)      | <1 day                  | global sulphur budget                                                                                                                                      |
| Junge (1963)                         | 1.7 days                | global sulphur budget                                                                                                                                      |
| Friend (1973)                        | 3.5 days                | global sulphur budget                                                                                                                                      |
| Cadle and Ledford<br>(1966)          | 2 hours                 | based on experimentally determined<br>reaction rates H <sub>2</sub> S + O <sub>3</sub> + SO <sub>2</sub> + H <sub>2</sub> O<br>in the presence of aerosols |
| Slatt <u>et al.</u> (1978)           | terrestrial 10-32 hours | based on Friend's estimates of H <sub>2</sub> S<br>production and concentrations<br>measured in study                                                      |
|                                      | marine 4-35 hours       |                                                                                                                                                            |
|                                      | global 7-33 hours       |                                                                                                                                                            |
|                                      | few minutes             | based on Cadle's reaction rates<br>and measured concentrations;<br>suggested as "improbable"                                                               |
| Stuhl (1974)                         | 30 hours                | reaction with OH radical at concen-<br>tration of $2.3 \times 10^{-6} \text{ cm}^{-3}$                                                                     |
| Jaeschke <u>et al.</u><br>(1978)     | 12.2 hours              | reaction with OH radical and<br>measured H <sub>2</sub> S concentrations                                                                                   |
| Carbon Disulphide (CS <sub>2</sub> ) |                         |                                                                                                                                                            |
| Sandalls & Penkett<br>(1977)         | 1 year                  | based on reaction with OH radicals<br>and measured concentrations                                                                                          |
| Dimethyl Sulphide (DMS)              |                         |                                                                                                                                                            |
| Cos (1975)                           | 0.8 days                | based on reaction with OH radicals                                                                                                                         |
| Lovelock <u>et al.</u><br>(1972)     | 7 days                  | suggested but not supported by any<br>evidence                                                                                                             |
| Methyl Mercaptan (MeSH)              |                         |                                                                                                                                                            |
| Cox (1975)                           | 0.09 days               | based on reaction with OH radicals                                                                                                                         |
| Carbonyl Sulphide (COS)              |                         |                                                                                                                                                            |
| Sandalls & Penkett<br>(1977)         | 20 years                | based on reaction with OH radicals                                                                                                                         |



Secondly, some transformation reactions, such as  $\text{H}_2\text{S}$  reactions with ozone and OH radicals (see Table 2-3), are not first order reactions and are incompatible with equation (1). As an example of the possible inaccuracy inherent in assuming a first order kinetic approximation, a global  $\text{H}_2\text{S}$  production of about  $430 \text{ TgSyr}^{-1}$  is obtained if an atmospheric residence time of 0.5 days (Jaeschke et al. 1978) and an average concentration of  $0.14 \text{ ugSm}^{-3}$  (Meszaros 1978) are substituted in equation (1). This production rate is double the biogenic release rates estimated by Junge (1963) and Eriksson (1963) (See Table 2-1).

The remaining portion of this section is concerned with the transformation mechanisms and residence times based upon experimental evidence.

Oxidation of hydrogen sulphide can proceed in cloud water droplets or in a homogeneous process such as reaction with ozone. Although the oxidation of  $\text{H}_2\text{S}$  in solution might proceed quite rapidly in cloud or fog droplets (Penkett 1972), the decay rate in this process is likely small compared to other mechanisms (Granat 1976). Ozone ( $\text{O}_3$ ), oxygen atoms ( $\text{O}$ ), molecular oxygen ( $\text{O}_2$ ) and hydroxyl radicals ( $\text{OH}$ ) may all react with  $\text{H}_2\text{S}$ .

Cadle and Ledford (1966) found there was a rapid reaction between  $\text{O}_3$  and  $\text{H}_2\text{S}$  in the presence of aerosols. However, Hales et al. (1974), who critically examined the estimated oxidation rate of  $\text{H}_2\text{S}$ , concluded this mechanism would result in a global  $\text{H}_2\text{S}$  lifetime of several weeks.

On a local basis Hitchcock (1977) found the occurrence of highest sulphate levels on days when ozone is trans-

ported downward from the upper troposphere and lower stratosphere. Her analysis indicated that much of the sulphate present appears to be from local biogenic sources associated with the distribution of wetlands. These observations support a relatively short lifetime for  $\text{H}_2\text{S}$  in the presence of increased levels of ozone. According to Hitchcock et al. (1978), under certain conditions  $\text{SO}_2$  was derived from the precursor  $\text{H}_2\text{S}$  and an unknown proportion of sulphate appeared to be of biogenic origin.

Stuhl (1974) and Cox (1975) estimated the reaction rate of  $\text{H}_2\text{S}$  with OH in the atmosphere. They arrived at atmospheric  $\text{H}_2\text{S}$  lifetimes of 1.3 and 2.3 days, respectively. Jaeschke et al. (1978), using Stuhl's (1974) reaction rates and their measured concentrations of  $\text{H}_2\text{S}$ , estimated the residence time to be about 0.5 days. Most of the recent evidence suggests a residence time of less than 1 day on a global basis and in some circumstances, such as in presence of elevated ozone levels, possibly in the order of a few hours or less.

Cox and Sandalls (1974) concluded that DMS is oxidized directly to sulphate by OH radicals and obtained an estimated residence time of 0.8 days (Cox 1975). The concentrations of DMS and  $\text{H}_2\text{S}$  (see Table 2-2) and their respective residence times in the atmosphere appear comparable; if this is so, it suggests that the production rates of DMS and  $\text{H}_2\text{S}$  are also comparable, at least over the ocean.

Carbonyl sulphide and carbon disulphide have relatively long residence times in the atmosphere (Sandalls and Penkett 1977), in contrast to a 2 hour lifetime estimated for methyl mercaptan (Cox 1975). According to Sandalls



and Penkett (1977), methyl mercaptan only has to be available in concentrations of the order of  $0.005 \text{ ugSm}^{-3}$  to account for 70 percent of the natural turnover of sulphur in the atmosphere. COS is possibly generated in the atmosphere by photolysis of  $\text{CS}_2$  (Sandalls and Penkett 1977) or from natural land or marine sources (Adams 1978).

From the available information, the following observations are of paramount importance in attempting to estimate sulphur fluxes from natural sources:

- i) hydrogen sulphide lifetimes in the atmosphere could conceivably vary from a few minutes to a few days depending upon the dominant transformation mechanism;
- ii) methyl mercaptan may have a very short lifetime in the atmosphere and could balance the atmospheric sulphur budget if present in concentrations of  $0.005 \text{ ugSm}^{-3}$ ;
- iii) current observed concentrations support the hypothesis that evolution of  $\text{H}_2\text{S}$  from natural sources balances the atmospheric sulphur budget if  $\text{H}_2\text{S}$  has a residence time comparable to methyl mercaptan or shorter;
- iv) production rates and/or residence times estimated in global budgets, assuming a steady state, are not accurate.

The actual  $\text{H}_2\text{S}$  reactions in the atmosphere must be resolved before accurate indications of the production of  $\text{H}_2\text{S}$  can be obtained from measurements of this compound in the atmosphere.





### 3. GENERATION MECHANISMS AND FLUX RATES OF NATURAL ATMOSPHERIC SULPHUR

#### 3.1 BIOGENIC SOURCES

##### 3.1.1 Terrestrial Processes

In most well drained soils, sulphur is present predominantly in the sulphate and organically combined forms. Sulphur levels vary considerably between regions and soil type. However, no detailed inventory of soil sulphur levels is currently available for Canada. In Manitoba soils, chernozems for example, have a low sulphur content and in fact may be sulphur deficient. Luvisols in Manitoba and Ontario are also frequently sulphur deficient.

Losses of sulphur from soils to the atmosphere have been known for some time, although the mechanisms have not been examined in detail. Siman and Janson (1976 b) showed losses of sulphur over a 35 day period varying between  $0.02 \text{ gSm}^{-2}$  for unfertilized soils, to between 0.2 and  $0.3 \text{ gSm}^{-2}$  for fertilized plots. The presence of plants increased the evolution of sulphur.

Natural sources of sulphur includes microbial anaerobic reduction of sulphate as well as direct losses from living, senescent and decaying vegetation. Methylation and other mineralization processes by bacteria can occur quite rapidly during the breakdown of soil organic matter and appear to account for a large part of the sulphur losses in anaerobic soils.

Releases from luvisols and brunisols, recorded by Adams (1978 a), Hitchcock et al. (1975), and Lovelock et al. (1972), included methylated organic compounds such as DMS and DMDS.  $H_2S$ , carbon disulphide and carbonyl sulphide were also produced. More limited information was available for podsol and chernozem soil types (Adams 1978 c) but similar compounds appeared to be evolved.

From the meagre data available, it appears that all terrestrial soils can produce a variety of volatile organic sulphur compounds and no consistent specific differences have been reported at this time. All soils, when wetted or under high moisture conditions, produced larger amounts of hydrogen sulphide. Under these conditions, organic sulphur emissions may be suppressed.

Lovelock et al. (1972) presented data from laboratory experiments on the emission of DMS from a variety of soils collected from various parts of the United States. No temperature or other soils information was given. Emission rates varied between 21 to  $84 \times 10^{-9} \text{ mg g}^{-1} \text{ hr}^{-1}$ . DMS production decreased in sealed flasks as carbon dioxide levels increased; this reaction with carbon dioxide may cause lower DMS evolution in anaerobic soils.

Adams (1978 b) has shown that most terrestrial soils produce some hydrogen sulphide even at field capacity (i.e. normal moisture conditions). In loams, silt loams and clay silts, it is produced in amounts similar to organic sulphur compounds. Hydrogen sulphide, DMS and DMDS fluxes from luvisols were an order of magnitude higher than from brunisols. Brunisols produced more carbonyl sulphide according to Adams et al. (1978 a) than other soil types. However, the maximum  $\text{COS-CS}_2$  flux of  $3.1 \text{ mgS/m}^2/\text{yr}$  was from brunisolic soils and contrasts with  $21.5 \text{ mgS/m}^2/\text{yr}$  from the marine sediment Cove Sound sampling locations. Data taken from Adams et al. (1978 a) are summarized as follows:



| Mean<br>Temperature<br>(°C) | Total S<br>(mgS/m <sup>2</sup> /yr) | Soil Type     | Production Rates<br>(mgS m <sup>-2</sup> yr <sup>-1</sup> ) |      |      |     |                 |
|-----------------------------|-------------------------------------|---------------|-------------------------------------------------------------|------|------|-----|-----------------|
|                             |                                     |               | H <sub>2</sub> S                                            | DMS  | DMDS | COS | CS <sub>2</sub> |
| 13                          | 1.39                                | Alluvial Clay | 0.14                                                        | 0.05 | -    | 1.2 | -               |
| 17                          | 7.7                                 | Luvisol       | 1.5                                                         | 1.5  | 3.4  | 0.3 | 1.0             |
| 12                          | 5.2                                 | Brunisol      | 0.37                                                        | 0.13 | 1.7  | 2.2 | 0.9             |
| 12                          | 3.4                                 | Organic       | -                                                           | 0.6  | 0.1  | 2.0 | 0.7             |

Levels of DMS and DMDS were higher in luvisolic soils, however, these soils had the highest ambient temperature which may account for some of the differences. These data confirm the findings of Hill et al. who showed extremely low hydrogen sulphide emissions below a temperature of 10°C. Night-time and day-time flux differences were also attributed, at least in part, to temperature. Although data are inadequate for significant conclusions, it appears that some consistent trends are emerging with higher DMDS and lower COS concentrations being recorded during daytime.

Total sulphur flux rates for different soil types are deficient in the literature. The most comprehensive studies were undertaken by Adams et al. (1978 a, b and c), whose work indicated a wide range in emission rates as follows:

|                 |             |                |
|-----------------|-------------|----------------|
| Luvisol         | 5.7 - 8.4   | Adams (1978 a) |
|                 | 16.9 - 17.0 | Adams (1978 b) |
|                 | 5.0 - 58.0  | Adams (1978 c) |
| Brunisols       | 3.0 - 5.1   | Adams (1978 a) |
|                 | 7.1 - 8.0   | Adams (1978 b) |
|                 | 8.0 - 90.0  | Adams (1978 c) |
| Podsols         | 13.0        | Adams (1978 c) |
| Chernozems      | 120.0       | Adams (1978 c) |
| Organic terrain | 0.0 - 3.4   | Adams (1978 a) |

All figures in mgS/m<sup>2</sup>/yr.

Most of Adams' work has dealt with soils which appear to be under some form of cultivation. Higher flux rates have been recorded by Siman and Jansson (1976 a & b) in a series of

pot experiments, but it is unclear how these can be related to field conditions. They recorded losses of 20 mgS/m<sup>2</sup>/35 day period under unfertilized conditions and about 200 mgS/m<sup>2</sup>/35 day period in conditions of high sulphur fertilization. Siman and Jansson's work would suggest that emission rates from the prairies, particularly Manitoba, could be underestimated in this study by an order of magnitude.

#### Aerobic Processes in Soils

The majority of volatile organic sulphur compounds are produced by aerobic methylation processes. DMS and DMDS have been detected in a wide variety of well drained soils by Adams et al. (1978 c), and are probably formed by methylation. (Lovelock et al. 1972, Challenger 1951). Carbon disulphide and carbonyl sulphide appear to be produced largely as breakdown products from proteins containing cysteine and cystine, although other processes may be involved (Banwart & Bremner 1975).

#### Anaerobic Processes in Soils

The principal processes which lead to the production of gaseous sulphur compounds under anaerobic conditions involve the reduction of sulphate to hydrogen sulphide by strains of the bacteria Desulfovibrio and Desulfotomaculatum. Jorgensen (1978) and Hansen et al. (1978) have shown that some hydrogen sulphide (3 per cent) originates from decomposition of organic sulphur.

The behaviour of sulphate-reducing bacteria in a wide variety of soils is well known (Hitchcock & Wechsler 1972) and includes data for muds, swamps, fens, marshes, bogs and periodically flooded lands (Burgeff 1961, Connell & Patrick 1968, Engler & Patrick 1973, Jorgensen 1977, Sparling & Hennick 1974, Takai & Kamura 1966, Vamos 1964, and others). These workers have shown that the release of hydrogen



sulphide from soils depends on the redox state, acidity, the supply of short chain organic compounds and the soluble iron concentration.

Concentrations showed a marked seasonal pattern with high levels occurring from May to July, then decreasing through late summer and fall. Concentrations peaked just below the soil surface and in some cases exceeded 15 mg  $\text{H}_2\text{S}$ /100 g of fresh soil (Hennick 1971, Sparling and Hennick 1974). Jorgensen (1977) also showed that peak sulphate reduction occurred between 1-4 cm below the surface of waterlogged sediments and up to 10 per cent of the hydrogen sulphide was precipitated as iron sulphides and not evolved to the atmosphere.

Metal sulphides appear to be relatively stable in anaerobic soils, with iron and manganese being least stable (Engler and Patrick 1975). However, it has been reported that levels in excess of 2000 ppm were required before significant loss to the atmosphere was recorded (Harter and McLean 1965).

The behaviour of hydrogen and metal sulphides is closely related to redox conditions. Harter & McLean (1965) showed that sulphide producing organisms become active at a redox of -75 mV and active growth occurs at -200 mV. Connell and Patrick (1966) showed that redox conditions of -150 mV are required for sulphide accumulation. These conditions occur only in gleysols and some organic soils. The oxidizing nature of the upper portions of gleysols may preclude large emissions of hydrogen sulphide.

Connell and Patrick (1966) report sulphide production from soils between pH 5.5 and 9.5. Review of other sources indicated some production between pH 4.2 and 10.4, however, significant accumulation of sulphide probably does not occur below the pH of 5.5 or 6.0. This would seem to indicate that acid fibrosols, which have pH values between 3.6 and 4.6, are not major sources of hydrogen sulphide.

In summary, it appears that while waterlogged organic soils have a high potential for sulphur emission, edaphic conditions frequently preclude the evolution of large amounts of hydrogen sulphide. Increased acidity in mesisols and fibrosols and the fixing or oxidation of hydrogen sulphide act to reduce sulphur emission rates. Sulphur production is restricted by temperatures less than 10°C and reaches significant levels only in excess of 20°C. This would indicate low sulphur production in cryboreal, subarctic and arctic soil climates.

Wetlands, marshes and reed swamps have probable emission rates between 1 and 30 mgS m<sup>-2</sup> yr<sup>-1</sup>. Muck soils in eutrophic wetlands have high emission rates averaging between 2 and 15 mgS m<sup>-2</sup> yr<sup>-1</sup> with higher rates under conditions where decomposition is occurring rapidly. Soils with high fines content frequently have lower recorded emission rates 1 - 3 mgS m<sup>-2</sup> yr<sup>-1</sup>, possibly because of slow diffusion rates, and re-oxidation or fixation by iron or manganese.

Many wetland soils are distributed in the northern boreal or cryoboreal soil climates and are thus low producing sites. Acid peats (fibrosols) produce low levels of sulphur 0 - 4 mgS m<sup>-2</sup> yr<sup>-1</sup> although the local dominance of this soil type may lead to higher ranking.



### 3.1.2. Aquatic Processes

In most oxygenated waters, sulphur is present primarily as sulphate, in concentrations ranging from less than 1 mg l<sup>-1</sup> in lakes with low electrolyte levels, to in excess of 50,000 mg l<sup>-1</sup> in sulphate saline lakes. As such, the main release of sulphur to the atmosphere from these lakes could be regarded as being derived from evaporated spray during conditions of high wind. The traditional theory also includes biogenic emission of hydrogen sulphide as a more significant source.

Such hydrogen sulphide may be generated by two mechanisms, including the decomposition of organically-bound sulphur, as well as the reduction of inorganic sulphate under anaerobic conditions. Although Rasmussen (1974) indicated that considerable release occurred from organic sulphur, Hansen et al. (1978), Jorgensen et al. (1978) and others presented evidence strongly suggesting that sulphate reduction to sulphide is the predominant process in aquatic systems. This process occurs rapidly under anaerobic conditions, but may also take place in aerobic sediments in small anaerobic interstices.

Decomposition of organically bound sulphur produces a wide variety of volatile sulphides, including dimethyl sulphide (DMS), dimethyl disulphide (DMDS), methanemercaptan (MeSH), and probably small amounts of carbon disulphide and carbonyl sulphide (Adams et al. 1978 a). Other organic sulphides and mercaptans have been tentatively identified but their chemical structure has not yet been confirmed (Adams pers. comm.).

Few data are available for organic sulphur compounds. DMS was not detectable in air but was measured as  $1.2 \times 10^{-5}$  mg m<sup>-3</sup> in the Atlantic Ocean off the coast of England (Love-lock et al. 1972). Atmospheric concentrations of other



volatile compounds have received less attention due to short residence times and extremely low concentrations.

Most research has been oriented towards measurements of emission rates and fluxes. Information is available for exchanges across sediment-water, sediment-air and water-air interfaces. Estimates of sulphur emission rates to the atmosphere by different researchers are characterized by a great deal of variation which results from variations in experimental techniques and test environments.

Factors causing variations in emission rates are numerous, they include air and surface temperature, wind speed, atmospheric ventilation (Hitchcock et al. 1977), vertical mixing, concentration gradients, diffusion rates and gas solubilities, oxygen concentrations in water, water depth overlying the anaerobic layer, light (photosynthesis level) and the rate of sulphate reduction. Adams et al. (1978 b) have demonstrated emission rate changes from 0.03 to 7.0  $\text{gSm}^{-2} \text{yr}^{-1}$  induced by temperature increases from 17.5°C through to 34°C. Zero emission rates are characteristic of snow and ice cover. Seasonal emission rates varied largely with mean temperature changes.

Biogenic sulphur emissions are related to primary production (Hitchcock 1975), either by the aerobic production of methylated sulphur forms during normal metabolism, or by  $\text{H}_2\text{S}$  and DMS production during anaerobic decomposition of organic residues.

In aerobic waters, hydrogen sulphide is rapidly oxidized to sulphate and therefore does not normally occur in significant concentrations. Hydrogen sulphide may also be re-oxidized to sulphate in the upper sediment layers by aerobic bacteria and algae. Release of hydrogen sulphide to the atmosphere is virtually zero if anaerobic sediments or anoxic hypolimnetic conditions are overlain by oxygen-



ated water. Recent studies have indicated that a 10 cm water layer almost completely reduced hydrogen sulphide release to the atmosphere (Jorgensen 1978). In lakes and oceans, it appears probable that only under conditions of strong vertical water movement would  $H_2S$  be released to the atmosphere from anaerobic bottom waters.

The general conclusion which arises from these studies is that  $H_2S$  is released from oxygen deficient waters, from wet areas with only 2-5 cm of water cover, from exposed sediments, and from turbulent littoral or coastal regions.

Measurements of actual values in the air or at the air-water interface are limited because of the extremely low levels and the problems of sampling and detecting these concentrations. Junge (1963) reported atmospheric concentrations ranging between 2 to  $20 \mu g m^{-3}$  for nearshore marine areas, while levels above polluted marine shorelines approached the odour limit of  $200 \mu g m^{-3}$ . Georgii (1976) recorded concentrations of  $0.6 \mu g m^{-3}$  at the surface of a shallow estuarine area which decreased to 0.1 to  $0.2 \mu g m^{-3}$  at a height of one meter, and levels of  $0.38 \mu g H_2S m^{-3}$  in sea water.

Emission rates vary considerably, with highest  $H_2S$  production occurring in highly productive estuarine ecosystems, swamps and marsh areas. Adams et al. (1978 a) measured flux rates within marine coastal areas which included exposed mudflats, estuarine swamps and marsh areas. The recorded  $H_2S$  emission rates ranged widely.

| <u>Emission rate</u><br>( $mg Sm^{-2} yr^{-1}$ ) | <u>Author</u>                 |
|--------------------------------------------------|-------------------------------|
| 1.75-44.2x10 <sup>4</sup>                        | Hansen <u>et al.</u> (1978 b) |
| 19.4                                             | Adams <u>et al.</u> (1978 b)  |
| 24.5-33.3                                        | Georgii (1976)                |
| 6.44x10 <sup>4</sup>                             | Adams <u>et al.</u> (1978 a)  |
| 1.39x10 <sup>5</sup>                             | Adams <u>et al.</u> (1978 b)  |

Estimates of DMS emission are much less variable in marine coastal areas. Several authors have shown a variation between 3.8 and 14.4 mgS m<sup>-2</sup> y<sup>-1</sup> (Maroulis & Brandy 1977). Emission estimates for other volatile sulphur compounds are notably lacking and are generally restricted to the work of Adams et al. (1978 a and b). This appears to be a serious data gap since it does not permit comparisons. Adams' techniques are currently being questioned by other workers (Hitchcock pers. comm.). Flux rates for COS and CS<sub>2</sub> combined in intertidal zones have been recorded by Adams et al. (1978 a) as 21.5 mgS m<sup>-2</sup> y<sup>-1</sup> although another test gave a reading of 1.2 mgS m<sup>-2</sup> y<sup>-1</sup>.

From the available information, it appears that while considerable amounts of volatile organic compounds such as DMS and DMDS have been identified as originating from algae, marine and fresh water ecosystems, measured flux rates of up to 15 mgS m<sup>-2</sup> y<sup>-1</sup> indicate that such compounds play a secondary role to hydrogen sulphide (up to 4.4x10<sup>5</sup> mgS m<sup>-2</sup> y<sup>-1</sup>). Littoral and shoreline areas probably provide the major aquatic sulphur source. Mechanisms may involve the movement of surface sediments by wave action and subsequent deposition on rocks or beaches where rapid loss of sulphur compounds to the atmosphere could occur. Transfer of hypolimnetic sulphur to the atmosphere is unlikely to occur except during fall overturn or during winter storms. No seasonal field observations are available yet.



### 3.2 OTHER NATURAL SOURCES

#### 3.2.1 Sea Spray

Seawater contains about 2.5 milligrams of sulphate ( $\text{SO}_4^{=}$ ) per gram of water. Particles of sea salt formed by the breaking of bubbles have been identified as an important natural source of atmospheric sulphur. Myriads of bubbles, generated mainly by entrainment of air by white caps and wavelets, eject small droplets into the atmosphere immediately above the sea surface. If these droplets are less than 20 to 30  $\mu\text{m}$  in diameter, they will remain airborne long enough to be evaporated to aerosols. Eriksson (1960) has estimated that the annual global production of  $\text{SO}_4^{=}$  is 44 Tg, of which 10 percent passes over the continents.

Sea salt contributes significantly to precipitation sulphate levels in coastal areas. Sulphates of precipitation can be partitioned into components of probable sea and non-sea origin by using the bulk sea ratio  $\text{SO}_4^{=}/\text{Na}=0.25$  (Sverdrup *et al.* 1949). By assuming neither Na or  $\text{SO}_4^{=}$  from the ocean is lost preferentially, then the sea-salt  $\text{SO}_4^{=}$  can be determined by the bulk sea ratio if the sodium concentration is known.

The relative percentage contribution of sea-salt sulphate to total sulphate in precipitation in Canada is listed in Table 3-1. The sea-salt sulphate fraction in the coastal provinces is substantially larger than in the continental interior. In Ontario and Quebec there are substantial

TABLE 3-1

## PERCENT CONTRIBUTION OF SEA-SALT SULPHATE IN WET DEPOSITION

| Province/District | Annual | Dec.-Feb. | Mar-May | June-Aug. | Sept.-Nov. |
|-------------------|--------|-----------|---------|-----------|------------|
| Newfoundland      | 12     | 23        | 10      | 3         | 12         |
| Nova Scotia       | 16     | 31        | 16      | 4         | 17         |
| New Brunswick     | 10     | 29        | 9       | 1         | 6          |
| Quebec            | 6      | 11        | 6       | 2         | 3          |
| Ontario           | 3      | 9         | 2       | 2         | 3          |
| Manitoba          | 3      | 4         | 2       | 2         | 3          |
| Saskatchewan      | 8      | 18        | 4       | 6         | 6          |
| Alberta           | 5      | 11        | 6       | 2         | 3          |
| British Columbia  | 13     | 20        | 10      | 5         | 15         |

\* based on CANSAP data for the period April 1977 to March 1978.



increases in precipitation sulphate concentrations from anthropogenic sources (R.L. Berry 1979) which also reduces the relative contribution of sea-salt sulphates. In northern Ontario, the relative contribution of sea-salt sulphate on an annual basis is about 6 percent, while in Southern Ontario it is about 1 percent.

As might be expected, the rate of sulphate sea-salt production is highly dependent on wind speed (Toba 1961, Woodcock 1953). For the coastal provinces, larger contributions to the sea-salt sulphate fraction occur during the winter months. In this period, there is increased cyclonic activity both in the Maritimes and off the coast of British Columbia, accompanied by higher windspeeds and subsequent increased sea-salt production.

The removal of sea-salt particles from the atmosphere has been measured at various distances inland from coastlines. Lodge (1955) reported decreases of greater than 10 times in sea particle concentrations 160 kilometres inland from the coast of Puerto Rico. Tsimogami (1975) identified a one half depletion of sea salt particle concentration at 20 to 25 km inland from the coasts of Japan. The removal of sea-salt particles as they are advected inland occurs by either wet or dry deposition. In England, Martin and Barber (1978) found sulphate sea-salt aerosols contributed similar amounts, under dry and wet conditions, to inland deposition gauges, but a much greater proportion in wet conditions at coastal locations. The relative amount of deposition in wet and dry conditions varies according to the climate.

Table 3-2 presents sea-salt sulphate concentrations observed over the ocean and on continents.

TABLE 3-2

## SEA-SALT SULPHATE CONCENTRATIONS IN AIR

| <u>Reference</u>               | <u>SO<sub>4</sub><sup>=</sup><br/>Concentration</u>                                                         | <u>Location</u> | <u>Comments</u>                                                                                                                        |
|--------------------------------|-------------------------------------------------------------------------------------------------------------|-----------------|----------------------------------------------------------------------------------------------------------------------------------------|
|                                |                                                                                                             |                 | Measured concentrations at 15 m height                                                                                                 |
| Gravenhorst & Jendrieke (1974) | 1. 0.01-0.07 $\mu\text{g}/\text{m}^3$<br>2. 0.2 $\mu\text{g}/\text{m}^3$<br>3. 0.5 $\mu\text{g}/\text{m}^3$ | N. Atlantic     | 1. at wind force 3<br>2. at wind force 4<br>3. at wind force 5.5<br>sea-salt sulphate concentrated in 1-10 $\mu$ radius particle size. |
| Gillette & Bedford (1971)      | 0.7 $\mu\text{g}/\text{m}^3$                                                                                | Pacific Ocean   | near-surface concentration may contain "excess" SO <sub>4</sub> <sup>=</sup> .                                                         |
| Friend (1973)                  | 0.77 $\mu\text{g}/\text{m}^3$                                                                               | all oceans      | average estimated global concentration.                                                                                                |
|                                | 0.19 $\mu\text{g}/\text{m}^3$                                                                               | land            | average estimated global concentration.                                                                                                |
| Granat (1976)                  | 0.1-0.5 $\mu\text{g}/\text{m}^3$                                                                            | N. Atlantic     | clean ocean background.                                                                                                                |

Values of sulphate concentrations except those by Gravenhorst and Jendrieke (1974) usually contain an excess sulphate attributed to either natural or anthropogenic gaseous precursors with values ranging from 0.4 to 1.4  $\mu\text{g m}^{-3}$  (Gravenhorst 1978). Gravenhorst and Jendrieke's (1974) data show larger sea-salt sulphate concentrations with increased wind speed. To obtain an estimate of sea-salt sulphate production as a function of windspeed, relations developed for sea salt production rates were scaled by the bulk sea water ratio of sodium to sulphate. The following is a description of the estimate methodology.

Toba (1965) used data from Durbin and White (1961) and



Woodcock (1953, 1957) to calculate the wind dependence of sea-salt production. For sea-salt particles of mass  $1 \times 10^{-9.5}$  grams, Toba determined the following sea-salt production rates:

$$\log F = 0.05V - 1.56 \quad V \geq 9$$

$$F = 0.08 \quad \text{for } V = 7$$

$$= 0.058 \quad = 6$$

$$= 0.02 \quad = 4$$

where  $F$  is the production rate in  $\text{cm}^{-2} \text{sec}^{-1}$

$V$  is the wind speed in  $\text{msec}^{-1}$

A particle mass of  $1 \times 10^{-9.5}$  grams corresponds to an aerosol radius of about 2 to 4  $\mu\text{m}$ , the size interval in which the major portion of sea-salt sulphate mass is found (Gravenhorst 1974). The residence time of aerosols of this size range is greater than 6-12 hours (Toba 1965). Toba did not obtain values for windspeeds less than  $4 \text{ m sec}^{-1}$ . A rough approximation may be obtained for  $3 \text{ m sec}^{-1}$  by assuming that the ratio of observed concentrations is proportional to rate of production at different wind speeds. Using this value and sea-salt concentrations determined by Lovett (1978) during light wind observations, sea-salt production at  $3 \text{ m sec}^{-1}$  ( $11 \text{ Km hr}^{-1}$ ) is estimated to be about  $0.015 \text{ cm}^{-2} \text{sec}^{-1}$ .

The proportion of sea water sulphate can now be estimated from the sea-salt production rate as sodium by scaling the flux rate by the bulk sea water ratio of  $\text{Na}/\text{SO}_4 = 0.25$ . Using these assumptions, estimates of sea-salt sulphate flux rates were determined for various wind speeds (see Table 3-3).

TABLE 3-3

## SEA-SALT SULPHATE PRODUCTION AS A FUNCTION OF WINDSPEED

| Windspeed                                |    | Sea-Salt<br>Particle Production<br>Rate | Sea-Salt Sulphate<br>Production Rate                   |                                         |
|------------------------------------------|----|-----------------------------------------|--------------------------------------------------------|-----------------------------------------|
| (msec <sup>-1</sup> Kmhr <sup>-1</sup> ) |    |                                         | (mgSO <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> ) | (mgSm <sup>-2</sup> day <sup>-1</sup> ) |
| 3                                        | 11 | 0.015                                   | 0.41                                                   | 0.14                                    |
| 4                                        | 14 | 0.02                                    | 0.54                                                   | 0.18                                    |
| 5                                        | 18 | 0.035                                   | 0.95                                                   | 0.32                                    |
| 6                                        | 22 | 0.058                                   | 1.56                                                   | 0.52                                    |
| 7                                        | 25 | 0.08                                    | 2.16                                                   | 0.72                                    |
| 10                                       | 36 | 0.09                                    | 2.44                                                   | 0.81                                    |
| 15                                       | 54 | 0.15                                    | 4.06                                                   | 1.35                                    |
| 20                                       | 72 | 0.27                                    | 7.34                                                   | 2.45                                    |

Large freshwater lakes may also emit sulphate particles into the air by the same mechanism as the ocean. However, no observations of particle production have been made from freshwater lakes by the bubble bursting mechanism. An approximation of the sulphate production rate can be obtained by scaling the sea-salt sulphate production rates by the ratio of the lake SO<sub>4</sub> concentration to seawater SO<sub>4</sub> concentration. The lake emissions can then be calculated using the following formula:

$$F_{\text{LAKESO}_4} = \frac{\text{SO}_4\text{LAKE}}{\text{SO}_4\text{SEAWATER}} \times F_{\text{SEASO}_4}$$

where  $F_{\text{SEASO}_4}$  = sea salt sulphate production rate

SO<sub>4</sub>LAKE = sulphate concentration in lakewater

SO<sub>4</sub>SEAWATER = sulphate concentration in seawater



### 3.2.2. Volcanoes and Hotsprings

The sulphur compounds emitted by volcanoes are predominantly  $\text{SO}_2$  and  $\text{H}_2\text{S}$ , along with smaller amounts of  $\text{SO}_3$  and various other sulphates. Thermodynamic considerations of equilibria existing in magmas suggest that gaseous sulphur must be largely present in the form of sulphur dioxide and hydrogen sulphide (Naughton et al. 1963). The ratio of sulphur dioxide to sulphate in a primary fumarole often approaches 100 to 1 on a weight basis. Substantial oxidation of the  $\text{SO}_2$  and  $\text{H}_2\text{S}$  to  $\text{SO}_3$  may occur as the hot fumarole gases mix with atmospheric oxygen. The  $\text{SO}_3$  then reacts with water vapour to produce sulphuric acid droplets.

The percentages of various sulphur compounds and total sulphur emitted show large variations for different volcanoes and also for eruptions from a single volcano. The composition of volcanic gases is roughly 95%  $\text{H}_2\text{O}$ , 4%  $\text{CO}_2$  and 1%  $\text{SO}_2$  (expressed as molar percentages). Part of the sulphur emitted by volcanoes mixes with air while the remainder precipitates in the vicinity of the eruption.

Although the rate of emission of sulphate compounds from volcanoes, averaged over the earth and over time, is probably several orders of magnitude less than that from anthropogenic sources (Kellogg et al. 1972) the eruption of a large volcano will have a marked effect on the atmosphere over periods varying from a few days to several weeks. Currently, there are no active volcanoes in Canada (Geological Survey of Canada 1970). However, a significant proportion of sulphur compounds emitted outside the country are available for long distance transport.

Hot springs may be a source of hydrogen sulphide or sulphur dioxide emissions. Waters from springs at Jasper have a reported free  $\text{H}_2\text{S}$  content (cited in U.S.G.S. 1968), while values of  $\text{H}_2\text{S}$  of up to 35 mg/l have been reported elsewhere



in acidic hot springs. Alkaline hot springs do not contain any free  $H_2S$  whereas calcareous springs near neutrality may contain about 2.5 mg/l (Castenholz 1969). No emission rates are available for gaseous sulphur compounds from hot springs. Hosler and Kaplan (1966) calculated the yearly global sulphur emitted by hot springs to air and river runoff to be  $12TgSyr^{-1}$ . It is not known what percentage of this total is released to the air.

A rough estimate of the possible  $H_2S$  releases from hot springs were made by assuming that a certain proportion of the aqueous  $H_2S$  enters the atmosphere. Observations by Hansen et al. (1978) appear to indicate that 0.001 percent of the  $H_2S$  in water is transferred to the air at a temperature of  $20^{\circ}C$ .

The rate of transport of a substance through a medium by molecular diffusion is directly proportional to its diffusivity. As the temperature increases, the diffusivity of a gas in water also increases. For hot spring temperatures which are in the vicinity of  $80$  to  $100^{\circ}C$ , the diffusivity is about 4 to 5 times greater than at  $20^{\circ}C$ . Consequently, the movement of  $H_2S$  in hot springs to the water-air interface, where it is available for transfer to the atmosphere, is also increased by the same magnitude. This implies that up to 0.01 percent of the  $H_2S$  in hot springs may be released to the air. The hydrogen sulphide emission rate in terms of water flow rates can be expressed as

$$F_{H_2S} = Q \times C \times K$$

where  $Q$  = hot spring flow rate

$C$  = concentration of  $H_2S$  in hot springs

$K$  = transfer of constant ( $\sim 0.01\%$ )

Using this relation for a hot spring with a flow rate of  $500 \text{ l min}^{-1}$  and an  $H_2S$  concentration of  $2mgH_2S$  per litre of water the estimated annual emission rate is  $50 gH_2Syr^{-1}$ .





### 3.2.3. Soils Dust

An important fraction of atmospheric particulate loading comes from soils. Even weak winds raise particles of minerals which appear to be a constant component of the atmospheric background loading. For the most part, the sources are local and confined to arid or semi-arid terrain. This material settles from the atmosphere or is washed out by rain and then possibly re-entrained into the atmosphere many times over before eventually reaching the ocean (Cadle 1973). Little is known concerning the rate at which mineral matter, including sulphur compounds are introduced into the atmosphere.

Lodge et al. (1968) suggested that the high concentration of sulphate in precipitation in arid areas of the West, Midwest, and Northwest United States originates from soil dust carried aloft and entrained in river water. The authors noted that calcium carbonate and calcium sulphate occur in high concentrations in the top soil layer of arid zones. However, the average concentrations tend to vary inversely with the quantity of precipitation which does not support the hypothesis that increased sulphate concentrations are a result of wind entrainment of soil dust particles.

Values of sulphate in wet deposition reported by Drozdova et al. (1964) were also quite high, in the order of  $4\text{mg S l}^{-1}$ , and were accompanied by high calcium concentrations which suggested dusty atmospheric conditions. However, it is not clear whether this sulphate originates from gaseous sulphur compounds oxidized to sulphuric acid, or whether it relates to sulphate soil particles that have become suspended in the air. Granat (1976), reviewing this data, considers windblown dust as a contributing source to atmospheric-sulphur, at least in or near arid areas.



The production of soil dust is very variable in space and time depending on wind speed, precipitation and soil texture. On a regional scale, soil dust may provide a significant contribution to sulphur concentrations in rainwater (Selezna et al. 1967, Lodge 1968).

The global estimate of Granat (1976) was used to obtain a flux rate for Canada. Granat assumed that one third of the suspended particles from wind erosion are below 1  $\mu\text{m}$  in diameter and available for long distance transport. He then used the average sulphur content in weathered rock of 33% cited by Hallberg (1977), and the global soil dust estimate of Butcher and Charlson (1972) of  $200\text{Tgyr}^{-1}$ , to obtain a global emission of about  $0.2 \times 10^6 \text{MTSyr}^{-1}$ .

The major portion of the soil sulphur would be from arid and semi-arid regions which constitute about  $42 \times 10^6 \text{Km}^2$  of the earth's surface (Whittaker 1970). The area of semi-arid and subarid land in Canada is about  $0.2 \times 10^6 \text{Km}^2$  (Agriculture Canada 1977). Using the ratio of land surface areas, a rough estimate of the annual production of sulphur in Canada by wind erosion is  $500 \times 10^6 \text{gS}$  or  $.0005 \text{gSm}^{-2}\text{yr}^{-1}$  in semi-arid and subarid areas of Canada. These areas occur mainly in the southern Interior Plain of Saskatchewan and Alberta. Some small areas are located in the valleys of the British Columbia plateau.

#### 3.2.4. Forest Fires

Forest fires are a possible source of sulphur emissions to the atmosphere as indicated by the research of various authors. Vines et al. (1971) reported detectable  $\text{SO}_2$  from Australian bush-fires and Evans and Allen (1971) indicated that substantial losses of sulphur occur during the burning of natural vegetation. The amount of gaseous sulphur released is inversely proportional to the amount of basic materials present in combustible tissues and directly proportional to sulphur content in the combustible materials. If sufficient base is present, sulphur can be completely retained in a laboratory ashing of plant tissue (Rennie and Halsted 1977). Evans and Allen's studies (1971) and laboratory ashing (Rennie and Halsted 1977) indicated that there is only partial gasification of sulphur from tissue combustion with the remainder staying as ash in the form of basic sulphur.

Sulphur oxides have been reported to be released from wigwam burners utilizing wood waste (EPA 1976). From the available information, it appears that sulphur compounds can be released to the atmosphere during burning of vegetation in forest fires, although the actual rates have not been accurately determined.

Rennie and Halsted (1977) estimated a forest fire flux rate of  $400 \text{ Kg SO}_2 \text{ Km}^{-2}$  based on a combusted oven-dry wood density of  $4 \text{ MT ha}^{-1}$ . They arrived at this flux rate by considering observations of  $\text{SO}_2$  from Australian bush fires (Vines et al. 1971), losses of sulphur from natural burning vegetation (Evans and Allen 1971), and an average sulphur content of 0.15 percent for combusted tissues (Rennie 1972).

Sulphur dioxide release rates cited for wigwam burners are in the vicinity of  $0.05 \text{ Kg SO}_2 \text{ MT}^{-1}$  when burning wood refuse



with an approximate moisture content of 50% (U.S. Environmental Protection Agency 1976). Adjusted for oven-dry spruce which has a bulk density of about 0.4g/cc, this release rate would be in the vicinity of  $0.18 \text{ Kg SO}_2 \text{ MT}^{-1}$ . This value corresponds to a forest fire flux rate of  $70 \text{ KgSO}_2 \text{ Km}^{-2}$  assuming an oven-dry wood density of  $4 \text{ MT ha}^{-1}$ .

The above two estimates of sulphur flux rates from forest fires differ substantially, and in addition it has been hypothesized that the nature and amounts of gaseous emission are directly related to variable parameters such as fire intensity, direction relative to the wind and indirectly related to the rate at which the fire spreads (U.S. EPA 1976). A flux rate of  $200 \text{ Kg SO}_2 \text{ Km}^{-2}$  ( $100 \text{ KgS K}^{-2}$ ) intermediate between 70 and  $400 \text{ Kg SO}_2 \text{ Km}^{-2}$  was chosen as an average flux rate in lieu of more definitive data. This value was applied to data on forest fire occurrence in Canada to obtain annual sulphur emission levels (see Section 4).

#### SULPHUR PRODUCTIVITY RANKING

Typical Flux Rate Limited  
( $\text{gS m}^{-2} \text{ yr}^{-1}$ )

| Flux Rate | Rank |
|-----------|------|
| $10^4$    | 1    |
| $10^3$    | 2    |
| $10^2$    | 3    |
| $10^1$    | 4    |
| $10^0$    | 5    |
| $10^{-1}$ | 6    |
| $10^{-2}$ | 7    |
| $10^{-3}$ | 8    |
| $10^{-4}$ | 9    |
| $10^{-5}$ | 10   |

Flux rates for area sources usually vary with a climatic parameter (i.e., sulphate reduction by bacteria is temperature dependent). A source that is limited in a certain





#### 4. SULPHUR EMISSION RATES AND PRODUCTIVITY RANKING

##### 4.1 SULPHUR PRODUCTIVITY RANKING

The variability of sulphur flux rates into the air from natural sources ranges over 8 orders of magnitude. For soils and coastal areas, Adams (1978c) cites values from  $0.001 \text{ gS m}^{-2} \text{ yr}^{-1}$  to  $2000 \text{ gS m}^{-2} \text{ yr}^{-1}$ . To encompass this wide range of fluxes, a sulphur productivity ranking based on a logarithmic scale was adapted in this study (Table 4-1).

TABLE 4-1

##### SULPHUR PRODUCTIVITY RANKING

| Upper Flux Rate Limited<br>( $\text{gS m}^{-2} \text{ yr}^{-1}$ ) | Rank |
|-------------------------------------------------------------------|------|
| $10^4$                                                            | 1    |
| $10^3$                                                            | 2    |
| $10^2$                                                            | 3    |
| $10^1$                                                            | 4    |
| $10^0$                                                            | 5    |
| $10^{-1}$                                                         | 6    |
| $10^{-2}$                                                         | 7    |
| $10^{-3}$                                                         | 8    |
| $10^{-4}$                                                         | 9    |
| $10^{-5}$                                                         | 10   |

Flux rates for area sources usually vary with a climatic parameter (i.e., sulphate reduction by bacteria is temperature dependent). A source that is classed in a certain

rank represents the sulphur productivity normalized to a base value of the main controlling factor - in the case of soils, the base emission rate chosen was typical of the growing season. These ranks were subsequently adjusted for different soil climates in Canada before estimating emissions. The emission rates and ranks by source are identified in the next two sections.

#### 4.1 SULPHUR PRODUCTIVITY RANKING

The variability of sulphur flux rates into the air from natural sources ranges over 3 orders of magnitude. For soils and organic wastes, which (1978) also range from 0.001 to 0.1 kg S m<sup>-2</sup> yr<sup>-1</sup>, it is necessary to use wide ranges of fluxes. A sulphur productivity ranking based on a logarithmic scale was adopted in this study (Table 4-1).

TABLE 4-1

#### SULPHUR PRODUCTIVITY RANKING

Upper Flux Rate Limit

| Rank | kg S m <sup>-2</sup> yr <sup>-1</sup> |
|------|---------------------------------------|
| 1    | 10 <sup>0</sup>                       |
| 2    | 10 <sup>1</sup>                       |
| 3    | 10 <sup>2</sup>                       |
| 4    | 10 <sup>3</sup>                       |
| 5    | 10 <sup>4</sup>                       |
| 6    | 10 <sup>5</sup>                       |
| 7    | 10 <sup>6</sup>                       |
| 8    | 10 <sup>7</sup>                       |
| 9    | 10 <sup>8</sup>                       |
| 10   | 10 <sup>9</sup>                       |

Flux rates for each source usually vary with climate (e.g., sulphate reduction by bacteria is temperature dependent). A source that is classified in a certain



## 4.2 BIOGENIC SOURCES

### 4.2.1 Soils

Following the system described in Table 4-1, ranks for major soil types were estimated from flux data reported by Adams (1978a,b,c), Hitchcock (1975) and Lovelock (1972):

| <u>Soil Type</u> | <u>EAG Ranking</u> |      | <u>Adams Ranking</u><br>(1978a) |
|------------------|--------------------|------|---------------------------------|
|                  | Range              | Mean |                                 |
| Luvisols         | 6-8                | 7    | 6                               |
| Brunisols        | 6-8                | 7    | 7                               |
| Podsols          | 7                  | 7    | 8                               |
| Chernozems       | 6-7                | 6-7  | -                               |
| Gleysols         | 5-6                | 5-6  | 4                               |
| Organic Terrain  | 3-9                | 5-6  | 2                               |
| Alluvial soils   | 4-7                | 6    | 5                               |
| Saline marshes   | 2-7                | 3-6  | 1                               |

The proposed ranking appeared to be rather insensitive to differences in soil types compared to the ranking proposed by Adams (1978a). However, that system was subjective and distinguished between fairly similar soil types such as brunisols and podsols.

The soil classifications used in this study were based upon those specified by the Soils Survey of Canada (Agriculture Canada 1977). These soil classifications, along with their estimated sulphur productivity ranking, related to the most commonly recorded flux rate during the growing season, are presented in Table 4-2.

Since measured flux rates appear to vary by several orders of magnitude with seasonality and location, the rankings are considered provisional until further field and laboratory studies can be undertaken. The ranks presented were adjusted to differences in soil conditions as follows.

TABLE 4-2

## SOIL CLASSIFICATIONS AND SULPHUR PRODUCTIVITY RANKINGS

|               |       |                    | <u>RANK</u> |
|---------------|-------|--------------------|-------------|
| A Chernozemic | A1    | Brown              | 7           |
|               | A2    | Dark Brown         | 6           |
|               | A3    | Black              | 6           |
|               | A4    | Dark Gray          | 7           |
| B Solonetzic  | B1 B2 | Solonetz           | 6           |
|               | B4    | Solod              | 6           |
| C Luvisolic   | C1    | Gray Brown luvisol | 7           |
|               | C2    | Gray luvisol       | 7           |
| D Podzolic    | D1    | Humic Podzol       | 6           |
|               | D2    | Ferro-Humic Podzol | 7           |
|               | D3    | Humo-Ferric Podzol | 7           |
| E Brunisolic  | E1    | Melanic Brunisol   | 7           |
|               | E2    | Eutric Brunisol    | 7           |
|               | E2    | Sombric Brunisol   | 7           |
|               | E3    | Dystric Brunisol   | 6           |
| F Regosolic   | F     | Regosolic          | 7           |
| G Gleysolic   | G1    | Humic Gleysol      | 5           |
|               | G2    | Gleysol            | 6           |
|               | G3    | Eluviated Gleysol  | 6           |
| H Organic     | H1    | Fibrosol           | 6           |
|               | H2    | Mesisol            | 3-5         |
|               | H3    | Humisol            | 3-5         |
| R Rockland    |       |                    | 8           |



1. Soils with higher organic and moisture contents have been ranked slightly higher.
2. Soils seasonally or continuously waterlogged have been ranked higher.
3. Soils with low porosity and aerobic horizons have been ranked slightly lower.
4. Acidic soils such as some fibrosols are ranked lower, since organisms producing volatile sulphur compounds grow slower below pH 5.5.

Corrections to the rankings are required for different mean temperature and soil climate conditions in Canada. Organisms involved in hydrogen sulphide and other volatile organic sulphur production (Adams 1978 a,b and c) are sensitive to temperature, with extremely lower production rates below 10°C. Adams (loc.cit.) has identified a ten fold increase in activity between 15 and 20 and between 20 and 30 degrees. Using these data, soils ranking adjustments according to soil climate were formulated as follows:

|                             |                                    |
|-----------------------------|------------------------------------|
| Reduction of 1 to 2         | Arctic and subarctic soil climates |
| Reduction of 1              | Cryoboreal soil climates           |
| No reduction or less than 1 | Boreal soil climates               |
| Rank remains unchanged      | Mesic soil climates                |

A preliminary estimate of Canadian sulphur emissions from soils was made from soils coverage data and derived sulphur productivity rankings (see Table 4-3).

TABLE 4-3

## PRODUCTION OF VOLATILE SULPHUR FROM CANADIAN SOILS

|   |             | Area<br>( $\times 10^3$ km) | Rank* | Maximum Sulphur<br>Production<br>(metric tons $\text{yr}^{-1}$ ) |
|---|-------------|-----------------------------|-------|------------------------------------------------------------------|
| A | Chernozemic |                             |       |                                                                  |
|   | Brown       | 100.6                       | 7     | 1010                                                             |
|   | Dark Brown  | 111.1                       | 6     | 11110                                                            |
|   | Black       | 200.7                       | 6     | 20070                                                            |
|   | Dark Gray   | 56.2                        | 7     | 560                                                              |
|   |             |                             |       | <hr/> 32750                                                      |
| B | Solonetzic  | 72.6                        | 6     | 7260                                                             |
| C | Luvisolic   | 809.3                       | 7     | 8090                                                             |
| D | Podzolic    | 2072.9                      | 7     | 20730                                                            |
| E | Brunisolic  |                             |       |                                                                  |
|   | Melanic     | 27.7                        | 8     | 30                                                               |
|   | Eutric      | 556.7                       | 7     | 5570                                                             |
|   | Dystric     | 382.2                       | 6     | 38220                                                            |
|   |             |                             |       | <hr/> 43820                                                      |
| F | Regosolic   | 2277.4                      | 7     | 22770                                                            |
| G | Gleysolic   | 213.2                       | 5-6   | 106600                                                           |
| H | Organic     | 927.4                       | 6     | 92740                                                            |
|   |             |                             |       | <hr/>                                                            |
|   | TOTAL       |                             |       | 334,760                                                          |

\* temperature correction was not applied for northern soil climates .

The total production of volatile sulphur from Canadian soils, estimated in Table 4-3, may reach  $0.33 \text{ TgS yr}^{-1}$ . This is likely an overestimate since a significant proportion of regosolic, gleysolic and organic soils are within northern soils climate regions (Alberta, Ontario) where sulphur production is likely much lower. The detailed estimate of sulphur emissions from soils on a county basis is tabulated in Section 5.



#### 4.2.2 Vegetation

Considerable evidence exists which would suggest that the presence of plants directly or indirectly effects the emission of sulphur. Lovelock et al. (1972) demonstrated that leaves of trees and herbs produced DMS in significant levels, which increased considerably during senescence. The annual primary production in terrestrial areas decreases northward with shorter growing seasons and lower temperatures. Productivity studies such as those by Westlake (1963) indicate that coniferous forests, deciduous forests and terrestrial herbs assimilate approximately 28, 12 and 20 metric tonnes  $\text{ha}^{-1} \text{yr}^{-1}$  respectively. Approximately 50 percent of these standing crops would be above ground.

Emission rates of DMS released from leaves, presented in Table 4-4, were estimated from flux rates measured by Lovelock et al. (1972) and the standing crop data of Westlake (1963).

TABLE 4-4

##### DMS EMISSION RATES FROM VEGETATION

| Type of Vegetation | Standing Crop<br>( $\text{gm}^{-2}$ ) | DMS Production<br>( $\text{gm}^{-2}\text{hr}^{-1}$ ) | DMS Production<br>( $10^{-6}\text{gm}^{-2}\text{yr}^{-1}$<br>for 180 days) |
|--------------------|---------------------------------------|------------------------------------------------------|----------------------------------------------------------------------------|
| Coniferous forest  | $14 \times 10^2$                      | $28 - 602 \times 10^{-10}$                           | 10.4 - 263.0                                                               |
| Deciduous forest   | $6 \times 10^2$                       | $12 - 258 \times 10^{-10}$                           | 5.2 - 112.7                                                                |
| Terrestrial forest | $10^3$                                | $20 - 430 \times 10^{-10}$                           | 8.7 - 188.0                                                                |

The figures in Table 4-4 suggest vegetation rankings between 8 and 10 which are several orders of magnitude lower than those determined for soils. During senescence, DMS evolution could be 2 to 3 times higher than that observed during the remainder of the year. Evolution of other volatile sulphur compounds by vegetation could also contribute to atmospheric loadings.

The rankings assigned to sulphur production from vegetation, based upon the estimates presented in Table 4-4 and adjusted for increased production during senescence, are as follows:

|                   | Rank   | Mean Rank |
|-------------------|--------|-----------|
| Coniferous forest | 9 - 7  | 8         |
| Deciduous forest  | 9 - 7  | 8         |
| Terrestrial herbs | 10 - 8 | 9         |

Since standing crops from arctic, subarctic and cryoboreal regions are lower (Westlake 1963; Pearsall and Gorham 1956), a reduction in rank would occur in some soil climates:

- i) Reduction of 2 for vegetation in arctic soil climates;
- ii) Reduction of 1 for vegetation in subarctic soil climates;
- iii) Reduction of zero to 1 for vegetation in cryoboreal soil climates.



Consideration of these soil climate ranking adjustments results in the following estimated sulphur productivity of vegetation in Canada:

| <u>Vegetation</u>               | <u>Soil Climate</u> | <u>EAG<br/>Ranking</u> |
|---------------------------------|---------------------|------------------------|
| Tundra                          | arctic              | 10                     |
| Tundra                          | sub-arctic          | 9                      |
| Coniferous and<br>mixed forests | boreal              | 7-8                    |
| Deciduous forest                | mesic               | 7-8                    |

These rankings were applied to measured areas of coverage by vegetation types for Canada to obtain an annual emission rate. The results of this estimate are given in Section 5.

An alternative method for assessing the role of vegetation in sulphur production is presented in Section 5. Provincial estimates of the sulphur emission for typical vegetation in each of the soil temperature climates indicate that boreal forest environments are important vegetational sulphur sources.

#### 4.2.3 Aquatic Systems

Volatile sulphur emissions from aquatic systems occur primarily from shoreline and littoral regions. The primary component appears to be hydrogen sulphide (Jorgensen et al. 1978; Hansen et al. 1978 ) which is produced in anaerobic muds and must diffuse through the water column before entering the atmosphere.

Several workers have shown that, because of the short life of hydrogen sulphide in aerobic water, emissions would be confined to lake margins. Hydrogen sulphide produced in deeper sediments would be oxidized to sulphate in the water column and could, in poorly buffered lakes, contribute significantly to the development of acidic hypolimnetic waters. Some production of volatile organic sulphur compounds such as DMS and DMDS is known to occur from various algae and also from the surface of lake or ocean water. However, the amount measured is generally small.

The freshwater biogenic classification has been based essentially upon the trophic status of the freshwater lakes, which may be categorized, according to the amounts of nutrients which they receive, into eutrophic, mesotrophic and oligotrophic systems.

Eutrophic lakes frequently develop anaerobic hypolimnetic conditions, a potential atmospheric sulphur source during the fall overturn. As well, these lakes may have nutrient rich muds in littoral and sublittoral regions.

Mesotrophic and oligotrophic lakes are poorer in nutrients and tend to be deeper. Marginal areas, such as the littoral zone, tend to be more restricted in representation. Potential sulphur productivity from such lakes may differ by more than an order of magnitude.



Lakes in northern regions of Canada often tend to be dystrophic, and have low overall productivity because of the acidic conditions, abundance of peat colloids, and low light penetration.

Following the ranking system (Table 4-1) values for major lake types were determined from the concentration and flux data reported by Jorgensen et al. (1978); Hansen et al. (1978) and others:

| Freshwater Biogenic Classifications and Sulphur Productivity Ranking |  |      |
|----------------------------------------------------------------------|--|------|
|                                                                      |  | Rank |
| 1. Rock shorelines                                                   |  | 10   |
| 2. Littoral Muds (exposed)                                           |  | 3-6  |
| 3. Swamps and Marsh shoreline                                        |  | 3-5  |
| 4. Eutrophic Lakes                                                   |  | 6    |
| 5. Mesotrophic Lakes                                                 |  | 7    |
| 6. Oligotrophic Lakes                                                |  | 8    |
| 7. Dystrophic and Bog Lakes                                          |  | 9    |

The total production of volatile sulphur from freshwater lakes, on a provincial basis, is tabulated in Section 5. The Canadian total is estimated as 11,850 metric tons per year.

Coastal areas have been classified according to Owen (1977) and rankings established on the basis of the shoreline characteristics within each of the marine divisions (Table 4-5). Total coastal sulphur emissions for each of the marine divisions are tabulated in Section 5.

Temperature corrections have been made for freshwater and coastal sources, using mean annual temperatures and the soil temperature classes following those outlined for soils and vegetation.

TABLE 4-5

MARINE BIOGENIC CLASSIFICATIONS AND  
SULPHUR PRODUCTIVITY RANKING

| I   | <u>Rock or Cliff Shores</u>                                 | RANK |
|-----|-------------------------------------------------------------|------|
|     | (1) exposed resistant coast with low backshore<br>or cliffs | 10   |
|     | (2) sheltered resistant coasts                              | 10   |
|     | (3) exposed unresistant cliffs                              | 10   |
|     | (4) sheltered unresistant cliffs                            | 10   |
| II  | <u>Shorelines With Beaches</u>                              |      |
|     | (5) cobble or mixed sediment beaches                        | 7    |
|     | (6) sand beaches                                            | 5    |
|     | (7) pocket beaches                                          | 4    |
|     | (8) sheltered beaches (lagoons)                             | 3-4  |
| III | <u>Shorelines With Intertidal Sediments</u>                 |      |
|     | (9) coarse sediments on a wave-cut platform                 | 4    |
|     | (10) intertidal mud                                         | 3-4  |
|     | (11) intertidal sand                                        | 3-4  |
| IV  | <u>Shorelines With Vegetation</u>                           |      |
|     | (12) marshes and swamps                                     | 2-4  |



### 4.3 OTHER SOURCES

#### 4.3.1 Sea and Lake Spray

Flux rates of sea salt sulphate production, as a function of windspeed, were estimated using derived sea salt production rates (Toba 1965) and scaling by the weight of sulphate contained in a sea salt particle. The estimated emission rates, as a function of windspeed, are as follows:

| <u>SO<sub>4</sub> Flux Rate</u><br><u>(gS m<sup>-2</sup> yr<sup>-1</sup>)</u> | <u>Windspeed</u><br><u>(Km hr<sup>-1</sup>)</u> |
|-------------------------------------------------------------------------------|-------------------------------------------------|
| 0.06                                                                          | 11                                              |
| 0.08                                                                          | 14                                              |
| 0.14                                                                          | 18                                              |
| 0.22                                                                          | 22                                              |

The annual mean windspeed in coastal areas in Canada usually ranges from 10 to 15 km hr<sup>-1</sup> (Canada Department of Transport 1968), so that a base sea salt sulphate flux rate of 0.07 gS m<sup>-2</sup> yr<sup>-1</sup> was selected. This rate corresponds to a sulphur productivity ranking of 6.

The sea salt emission rates, on an annual basis, for Canadian coastal areas were calculated by summing the individual seasonal contributions. If ice occurred during a season, it was assumed that no sea-salt sulphate production occurred in the area. Table 4-6 lists the annual emission rates derived for the major coastal areas in Canada.

$$\text{Emission Rate} = \text{ice-free period fraction} \times \text{area (m}^2\text{)} \\ \times 7 \times 10^{-2}$$

TABLE 4-6

SEA-SALT EMISSION RATES  
FOR COASTAL AREAS

|                | Windspeed<br>(Km hr <sup>-1</sup> ) | Sulphate Emission Rate<br>(gS m <sup>-2</sup> season <sup>-1</sup> ) |
|----------------|-------------------------------------|----------------------------------------------------------------------|
| Pacific Ocean  |                                     |                                                                      |
| Dec-Feb        | 17+                                 | 0.03                                                                 |
| Mar-May        | 13                                  | 0.02                                                                 |
| June-Aug       | 10                                  | 0.01                                                                 |
| Sept-Nov       | 12                                  | 0.01                                                                 |
|                |                                     | Annual 0.07                                                          |
| Atlantic Ocean |                                     |                                                                      |
| Dec-Feb        | 23                                  | 0.06                                                                 |
| Mar-May        | 21                                  | 0.06                                                                 |
| June-Aug       | 15                                  | 0.02                                                                 |
| Sept-Nov       | 19                                  | 0.03                                                                 |
|                |                                     | Annual 0.17                                                          |
| Labrador Sea   |                                     |                                                                      |
| Dec-Feb        | ice*                                |                                                                      |
| Mar-May        | ice                                 |                                                                      |
| June-Aug       | 14                                  | 0.02                                                                 |
| Sept-Nov       | 16                                  | 0.02                                                                 |
|                |                                     | Annual 0.04                                                          |
| Hudson Bay     |                                     |                                                                      |
| Dec-Feb        | ice                                 |                                                                      |
| Mar-May        | ice                                 |                                                                      |
| June-Aug       | 21 (½ ice)                          | 0.03                                                                 |
| Sept-Nov       | 27 (½ ice)                          | 0.04                                                                 |
|                |                                     | Annual 0.07                                                          |
| Beaufort Sea   |                                     |                                                                      |
| Dec-Feb        | ice                                 |                                                                      |
| Mar-May        | ice                                 |                                                                      |
| June-Aug       | 21                                  | 0.06                                                                 |
| Sept-Nov       | ice                                 |                                                                      |
|                |                                     | Annual 0.06                                                          |

+ wind data from Canada Department of Transport (1968)

\* ice data from Environmental Protection Service (1977)



Lake sulphate production by the sea spray mechanism was calculated by scaling the sea sulphate flux rate by the ratio of sulphate concentration in lake waters to that in sea water. An average lake water sulphate concentration of  $4 \text{ mgSO}_4\text{l}^{-1}$  was used to calculate the base rate (the average sea water sulphate concentration is  $2.5 \text{ gSO}_4\text{l}^{-1}$ ). Values of sulphur production as a function of windspeed are listed below:

| <u>SO<sub>4</sub> Flux Rate</u><br><u>(gS m<sup>-2</sup> yr<sup>-1</sup>)</u> | <u>Windspeed</u><br><u>(Km hr<sup>-1</sup>)</u> |
|-------------------------------------------------------------------------------|-------------------------------------------------|
| 0.0001                                                                        | 11                                              |
| 0.0001                                                                        | 14                                              |
| 0.0002                                                                        | 18                                              |
| 0.0004                                                                        | 22                                              |

These estimates of emission rates for lake sulphate sources are in the order of  $10^{-3}$  times smaller than sea-salt flux rates. A sulphate flux rate of  $0.0001 \text{ gS m}^{-2} \text{ yr}^{-1}$  was adopted which corresponds to a sulphur productivity ranking of 9. This rate was applied to lakes of  $1000 \text{ km}^2$  in area or larger based on the assumption that these lakes would have a sufficient fetch to produce substantial waves (see Section 5). The estimated lake emissions were multiplied by the ice-free period (no production of sulphate would occur with ice cover) to obtain the annual release.

#### 4.3.2 Soil Dust

A sulphur emission rate was derived for wind suspended soil particles from semi-arid and sub-arid land in Canada from the global estimate of Granat (1976). The emission rate for Canada was  $0.0005 \text{ gS m}^{-2} \text{ yr}^{-1}$  which corresponds to a sulphur productivity ranking of 8. The variability of this estimate is likely greater than an order of magnitude.



#### 4.3.3 Forest Fires

Forest fires may release sulphur dioxide at a rate of about  $1 \times 10^5$  gS for each square kilometre burned. In Canada an average of about 10,200 km<sup>2</sup> are burned annually, yielding an average annual emission rate of  $10^{-5}$  gS m<sup>-2</sup> yr<sup>-1</sup>. This emission rate corresponds to a sulphur productivity ranking of 10. Table 4-7 lists the annual emitted amounts of sulphur dioxide by province.

TABLE 4-7  
ANNUAL SULPHUR EMISSIONS FROM  
FOREST FIRES ( $10^6$  gS)

|                                    |      |
|------------------------------------|------|
| Newfoundland                       | 81   |
| Prince Edward Island               | -    |
| Nova Scotia                        | 3    |
| New Brunswick                      | 5    |
| Quebec                             | 60   |
| Ontario                            | 55   |
| Manitoba                           | 203  |
| Saskatchewan                       | 164  |
| Alberta                            | 64   |
| British Columbia                   | 171  |
| Yukon and Northwest<br>Territories | 194  |
| Canada                             | 1000 |

The sulphur emissions in any year will vary greatly depending on the number of forest fires. Values for the period 1971 to 1976 were calculated for Ontario and are listed in Table 4-8.

In severe years, Ontario alone can contribute over half the average sulphur emissions expected for Canada.

TABLE 4-8

SULPHUR EMISSIONS FROM FOREST FIRES  
IN ONTARIO, 1971-1976

| Year | Area Burned<br>(Km <sup>2</sup> ) | Sulphur Emissions<br>(10 <sup>6</sup> gSO <sub>2</sub> ) |
|------|-----------------------------------|----------------------------------------------------------|
| 1976 | 5470                              | 547                                                      |
| 1975 | 169                               | 17                                                       |
| 1974 | 5267                              | 527                                                      |
| 1973 | 36                                | 4                                                        |
| 1972 | 322                               | 32                                                       |
| 1971 | 147                               | 15                                                       |



#### 4.3.4 Miscellaneous

Hot springs are considered potential emitters of hydrogen sulphide. The annual release of sulphur was estimated to be about 5000 gS yr<sup>-1</sup> for hot springs located in British Columbia and Alberta. Volcanoes are large point sources of sulphur dioxide but no active volcanoes are present in Canada. However, the emitted gases and particles from volcanoes located abroad are transported over large distances, and do contribute to the natural atmospheric sulphur budget for Canada. However, due to the lack of data, no estimate of this contribution was made.





## 5. ANNUAL NATURAL SULPHUR EMISSIONS FOR CANADA

### 5.1 BIOGENIC EMISSIONS

This section presents the estimates of biogenic emissions from land and marine areas. Figure 1 provides an index to census division maps (Figures 2-7) and corresponding soil and marine classification maps (Figures 8-13). These latter maps also illustrate high (rank 5) and moderate (rank 5-6) sulphur productivity from marine and census divisions. These figures are appended to this report.





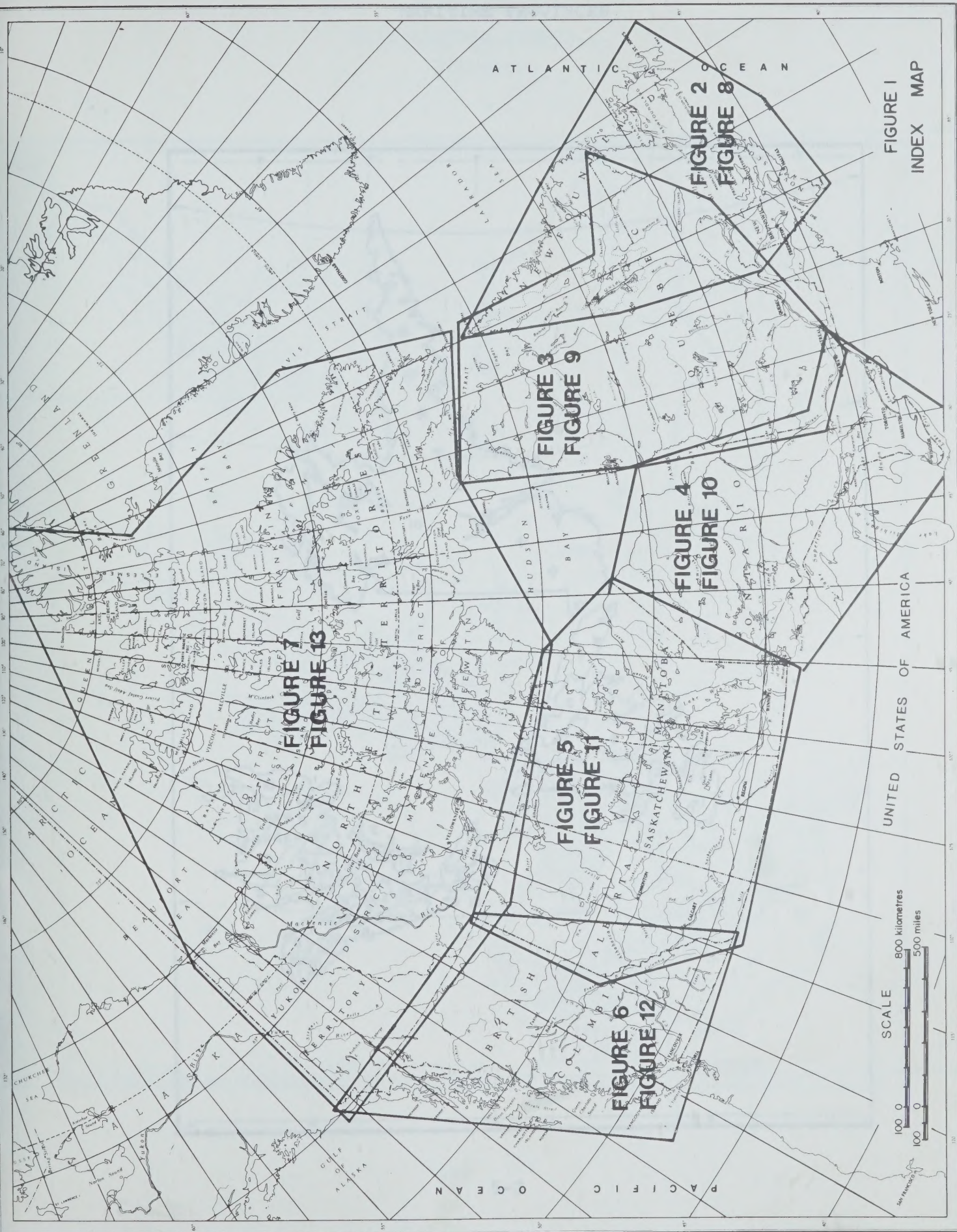
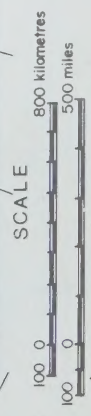


FIGURE 1  
INDEX MAP

UNITED STATES OF AMERICA









COUNTY DISTRIBUTION  
MARITIME PROVINCES

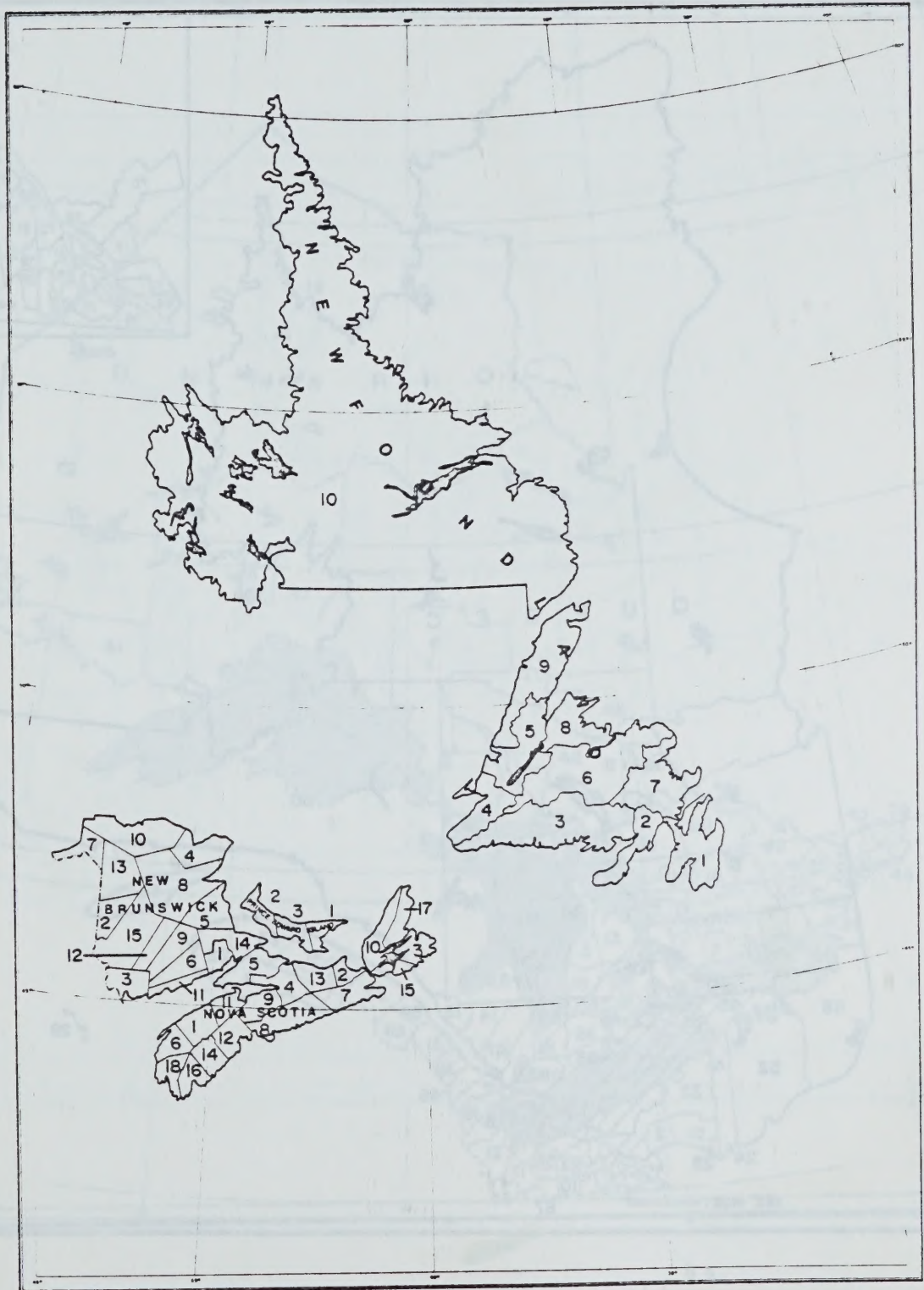


FIGURE 3  
COUNTY DISTRIBUTION  
QUEBEC





FIGURE 4  
COUNTY DISTRIBUTION  
ONTARIO



FIGURE 5  
COUNTY DISTRIBUTION  
PRAIRIE PROVINCES





FIGURE 6  
COUNTY DISTRIBUTION  
BRITISH COLUMBIA

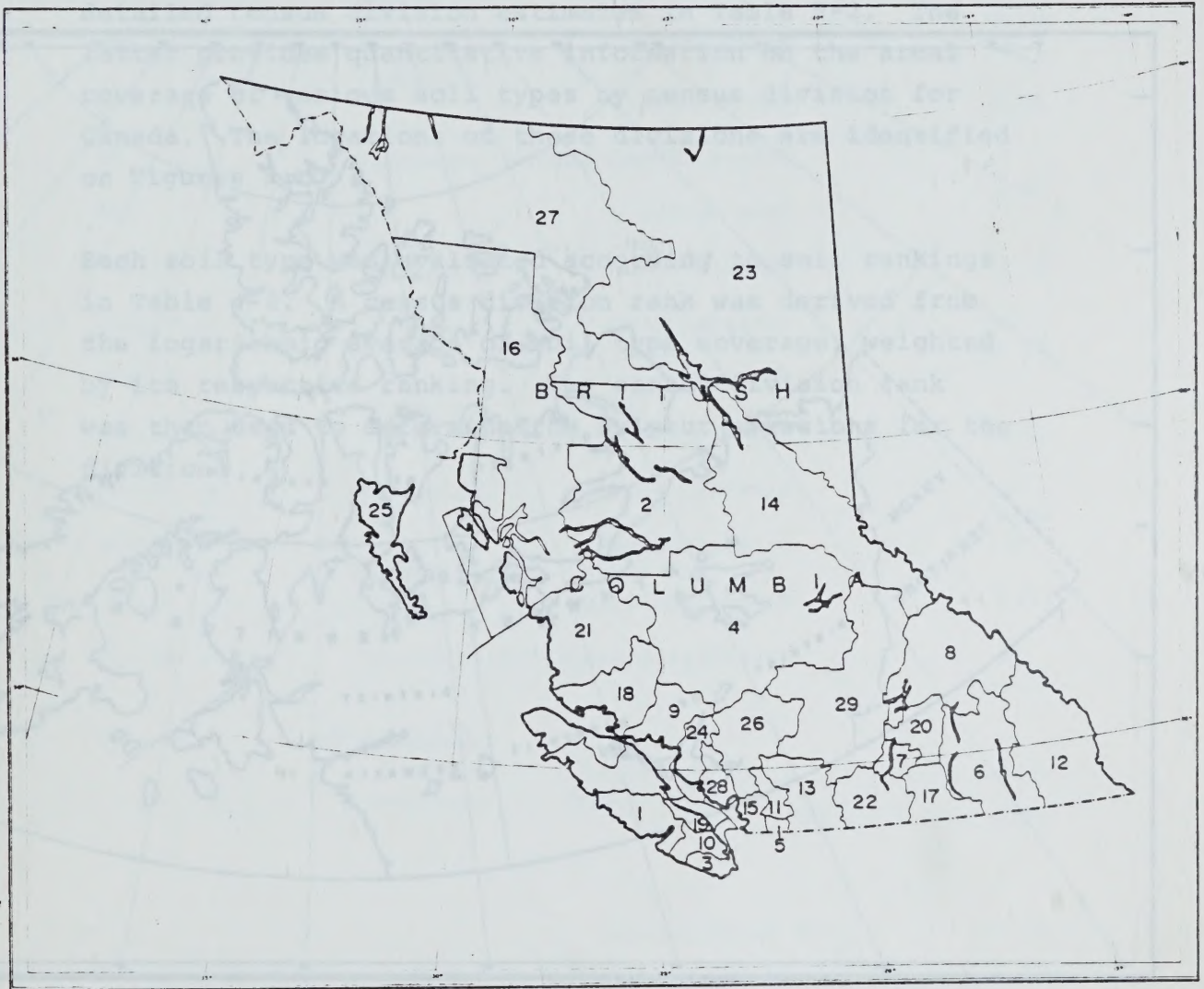


FIGURE 7  
DISTRICT DISTRIBUTION  
TERRITORIES





### 5.1.1 Soils

Tables of emissions estimates are provided for soils (Tables 5-1 and 5-2), vegetation (Table 5-3), and marine divisions (Tables 5-4 and 5-5). Table 5-1 is a provincial summary of sulphur emissions from soils obtained from the detailed census division estimates in Table 5-2. The latter provides quantitative information on the areal coverage of various soil types by census division for Canada. The locations of these divisions are identified on Figures 2 to 7.

Each soil type was evaluated according to soil rankings in Table 4-2. A census division rank was derived from the logarithmic average of soil type coverage, weighted by its respective ranking. The census division rank was then used to determine the sulphur emissions for the division.

TABLE 5-1

## ANNUAL EMISSIONS OF SULPHUR FROM SOILS

| <u>Provincial Summary</u> |                        |                                                        |
|---------------------------|------------------------|--------------------------------------------------------|
| <u>No.</u>                | <u>Province</u>        | <u>Annual Sulphur Emissions<br/>(metric tons as S)</u> |
| 1                         | Newfoundland           | 1,561                                                  |
| 2                         | New Brunswick          | 740                                                    |
| 3                         | Prince Edward Island   | 72                                                     |
| 4                         | Nova Scotia            | 606                                                    |
| 5                         | Quebec                 | 23,400                                                 |
| 6                         | Ontario                | 65,944                                                 |
| 7                         | Manitoba               | 47,860                                                 |
| 8                         | Saskatchewan           | 16,373                                                 |
| 9                         | Alberta                | 31,830                                                 |
| 10                        | British Columbia       | 27,976                                                 |
| 11                        | Yukon Territory        | 4,950                                                  |
| 12                        | North West Territories | 22,770                                                 |
| CANADA TOTAL              |                        | 244,082                                                |



TABLE 5-2

## COUNTY RANKING AND SULPHUR PRODUCTION

Newfoundland

| <u>No.</u> | <u>Census<br/>Division</u> | <u>Soil Type</u> | <u>Area<br/>(km<sup>2</sup>)</u> | <u>Rank</u> | <u>Division<br/>Rank</u> | <u>Sulphur<br/>Production<br/>(10<sup>7</sup>g yr<sup>-1</sup>)</u> |
|------------|----------------------------|------------------|----------------------------------|-------------|--------------------------|---------------------------------------------------------------------|
| 1          | --                         | podzolic         | 9,055                            | 7           | 7                        | 9.06                                                                |
| 2          | --                         | podzolic         | 6,305                            | 7           | 7                        | 6.31                                                                |
| 3          | --                         | podzolic         | 21,066                           | 7           | 7                        | 21.07                                                               |
| 4          | --                         | podzolic         | 5,455                            | 7           | 7                        | 7.39                                                                |
|            |                            | luvisolic        | 1,843                            |             |                          |                                                                     |
| 5          | --                         | podzolic         | 9,139                            | 7           | 7                        | 9.14                                                                |
| 6          | --                         | podzolic         | 18,130                           | 7           | 7                        | 18.13                                                               |
| 7          | --                         | podzolic         | 9,943                            | 7           | 7                        | 9.94                                                                |
| 8          | --                         | podzolic         | 9,539                            | 7           | 7                        | 9.54                                                                |
| 9          | --                         | podzolic         | 14,410                           | 7           | 7                        | 14.41                                                               |
| 10         | --                         | podzolic         | 61,897                           | 7           |                          |                                                                     |
|            |                            | organic          | 8,702                            | 6           |                          |                                                                     |
|            |                            | rockland         | 156,871                          | 8           | 7-8                      | 51.09                                                               |

Newfoundland Total 156.18

# COUNTY RANKS AND SULPHUR PRODUCTION

## Nova Scotia

| <u>No.</u> | <u>Census<br/>Division</u> | <u>Soil Type</u> | <u>Area<br/>(km<sup>2</sup>)</u> | <u>Rank</u> | <u>Division<br/>Rank</u> | <u>Sulphur<br/>Production<br/>(10<sup>7</sup> g yr<sup>-1</sup>)</u> |
|------------|----------------------------|------------------|----------------------------------|-------------|--------------------------|----------------------------------------------------------------------|
| 1          | Annapolic                  | podzolic         | 4094                             | 7           | 7                        | 4.09                                                                 |
| 2          | Antigonish                 | luvisolic        | 922                              | 7           |                          |                                                                      |
|            |                            | podzolic         | 819                              | 7           | 7                        | 1.74                                                                 |
| 3          | Cape Breton                | podzolic         | 2874                             | 7           | 7                        | 2.87                                                                 |
| 4          | Colchester                 | luvisolic        | 1536                             | 7           |                          |                                                                      |
|            |                            | podzolic         | 2355                             | 7           | 7                        | 3.89                                                                 |
| 5          | Cumberland                 | luvisolic        | 1536                             | 7           |                          |                                                                      |
|            |                            | podzolic         | 2559                             | 7           |                          |                                                                      |
|            |                            | regosolic        | 409                              | 8           | 7                        | 4.14                                                                 |
| 6          | Digby                      | podzolic         | 3071                             | 7           | 7                        | 3.07                                                                 |
| 7          | Guysborough                | luvisolic        | 205                              | 7           |                          |                                                                      |
|            |                            | podzolic         | 4505                             | 7           | 7                        | 4.71                                                                 |
| 8          | Halifax                    | luvisolic        | 4198                             | 7           |                          |                                                                      |
|            |                            | podzolic         | 1330                             | 7           | 7                        | 5.53                                                                 |
| 9          | Hauts                      | luvisolic        | 1741                             | 7           |                          |                                                                      |
|            |                            | podzolic         | 1638                             | 7           | 7                        | 3.38                                                                 |
| 10         | Inverness                  | luvisolic        | 1741                             | 7           |                          |                                                                      |
|            |                            | podzolic         | 2355                             | 7           | 7                        | 4.10                                                                 |
| 11         | Kings                      | luvisolic        | 102                              | 7           |                          |                                                                      |
|            |                            | podzolic         | 2253                             | 7           | 7                        | 2.35                                                                 |
| 12         | Lunenburg                  | podzolic         | 3481                             | 7           | 7                        | 3.48                                                                 |



# Nova Scotia (Cont'd)

|    |           |           |      |   |   |      |
|----|-----------|-----------|------|---|---|------|
| 13 | Pictou    | luvisolic | 1126 | 7 |   |      |
|    |           | podzolic  | 2150 | 7 |   |      |
|    |           |           |      |   | 7 | 3.28 |
| 14 | Queens    | podzolic  | 3174 | 7 |   |      |
|    |           |           |      |   | 7 | 3.17 |
| 15 | Richmond  | luvisolic | 1024 | 7 |   |      |
|    |           | podzolic  | 511  | 7 |   |      |
|    |           |           |      |   | 7 | 1.53 |
| 16 | Shelburne | podzolic  | 2867 | 7 |   |      |
|    |           |           |      |   | 7 | 2.87 |
| 17 | Victoria  | podzolic  | 2969 | 7 |   |      |
|    |           |           |      |   | 7 | 2.97 |
| 18 | Yarmouth  | podzolic  | 3379 | 7 |   |      |
|    |           |           |      |   | 7 | 3.38 |

Nova Scotia - Total 60.55

## COUNTY RANKS AND SULPHUR PRODUCTION

### PRINCE EDWARD ISLAND

| <u>No.</u> | <u>Census<br/>Division</u> | <u>Soil Type</u> | <u>Area<br/>(km<sup>2</sup>)</u> | <u>Rank</u> | <u>Division<br/>Rank</u> | <u>Sulphur<br/>Production<br/>(10<sup>7</sup> g yr<sup>-1</sup>)</u> |
|------------|----------------------------|------------------|----------------------------------|-------------|--------------------------|----------------------------------------------------------------------|
| 1          | Kings                      | podzolic         | 2253                             | 7           |                          |                                                                      |
|            |                            |                  |                                  |             | 7                        | 2.25                                                                 |
| 2          | Prince                     | podzolic         | 2354                             | 7           |                          |                                                                      |
|            |                            |                  |                                  |             | 7                        | 2.35                                                                 |
| 3          | Queens                     | podzolic         | 2560                             | 7           |                          |                                                                      |
|            |                            |                  |                                  |             | 7                        | 2.56                                                                 |

Prince Edward Island - Total 7.16

# COUNTY RANKS AND SULPHUR PRODUCTION

## New Brunswick

| <u>No.</u> | <u>Census<br/>Division</u> | <u>Soil Type</u>      | <u>Area<br/>(km<sup>2</sup>)</u> | <u>Rank</u> | <u>Division<br/>Rank</u> | <u>Sulphur<br/>Production<br/>(10<sup>7</sup> g yr<sup>-1</sup>)</u> |
|------------|----------------------------|-----------------------|----------------------------------|-------------|--------------------------|----------------------------------------------------------------------|
| 1          | Albert                     | luvisolic<br>podzolic | 409<br>1638                      | 7<br>7      | 7                        | 2.04                                                                 |
| 2          | Carleton                   | podzolic              | 3584                             | 7           | 7                        | 3.58                                                                 |
| 3          | Charlotte                  | podzolic              | 3585                             | 7           | 7                        | 3.58                                                                 |
| 4          | Gloucester                 | luvisolic<br>podzolic | 2150<br>2662                     | 7<br>7      | 7                        | 4.81                                                                 |
| 5          | Kent                       | luvisolic<br>podzolic | 3686<br>1229                     | 7<br>7      | 7                        | 4.91                                                                 |
| 6          | Kings                      | luvisolic<br>podzolic | 819<br>2458                      | 7<br>7      | 7                        | 3.27                                                                 |
| 7          | Madawaska                  | podzolic              | 3276                             | 7           | 7                        | 3.28                                                                 |
| 8          | Northumberland             | luvisolic<br>podzolic | 5018<br>737.2                    | 7<br>7      | 7                        | 10.38                                                                |
| 9          | Queens                     | luvisolic<br>podzolic | 1946<br>1434                     | 7<br>7      | 7                        | 3.18                                                                 |
| 10         | Restigouche                | podzolic              | 9010                             | 7           | 7                        | 9.01                                                                 |
| 11         | St. John                   | podzolic              | 1638                             | 7           | 7                        | 1.64                                                                 |
| 12         | Sunbury                    | luvisolic<br>podzolic | 1536<br>1126                     | 7<br>7      | 7                        | 2.66                                                                 |
| 13         | Victoria                   | podzolic              | 6450                             | 7           | 7                        | 6.45                                                                 |



New Brunswick (Cont'd)

|    |              |           |      |   |   |       |
|----|--------------|-----------|------|---|---|-------|
| 14 | Westmoreland | luvisolic | 2253 | 7 |   |       |
|    |              | podzolic  | 2765 | 7 |   |       |
|    |              | regosolic | 205  | 7 |   |       |
|    |              |           |      |   | 7 | 5.22  |
| 15 | York         | luvisolic | 1741 | 7 |   |       |
|    |              | podzolic  | 8294 | 7 |   |       |
|    |              |           |      |   | 7 | 10.03 |

New Brunswick - Total 74.04

# COUNTY RANKING AND SULPHUR PRODUCTION

## Québec

| <u>No.</u> | <u>Census Division</u> | <u>Soil Type</u> | <u>Area (km<sup>2</sup>)</u> | <u>Rank</u> | <u>Division Rank</u> | <u>Sulphur Production (10<sup>7</sup> g yr<sup>-1</sup>)</u> |
|------------|------------------------|------------------|------------------------------|-------------|----------------------|--------------------------------------------------------------|
| 1          | Abitibi                | luvisolic        | 10342                        | 7           |                      |                                                              |
|            |                        | podzolic         | 30205                        | 7           | 7                    | 40.54                                                        |
| 2          | Argenteuil             | brunisollic      | 1741                         | 6-7         |                      |                                                              |
|            |                        | gleysolic        | 205                          | 5-6         | 6                    | 19.46                                                        |
| 3          | Arthabaska             | podzolic         | 1740                         | 7           | 7                    | 1.74                                                         |
| 4          | Bagot                  | podzolic         | 715                          | 7           |                      |                                                              |
|            |                        | brunisollic      | 306                          | 6-7         | 7                    | 1.02                                                         |
| 5          | Beauce                 | podzolic         | 2665                         | 7           | 7                    | 2.67                                                         |
| 6          | Beauharnois            | brunisollic      | 205                          | 6-7         | 6-7                  | 1.03                                                         |
| 7          | Bellechasse            | podzolic         | 2457                         | 7           | 7                    | 2.46                                                         |
| 8          | Berthier               | podzolic         | 7373                         | 7           |                      |                                                              |
|            |                        | gleysolic        | 410                          | 5-6         | 6                    | 7.78                                                         |
| 9          | Bonaventure            | podzolic         | 512                          | 7           |                      |                                                              |
|            |                        | brunisollic      | 2367                         | 6-7         | 6-7                  | 14.40                                                        |
| 10         | Brome                  | podzolic         | 3072                         | 7           | 7                    | 3.07                                                         |
| 11         | Chambly                | podzolic         | 2048                         | 7           |                      |                                                              |
|            |                        | brunisollic      | 52                           | 6-7         |                      |                                                              |
|            |                        | gleysolic        | 51                           | 5-6         | 6-7                  | 10.75                                                        |
| 12         | Champlain              | podzolic         | 23653                        | 7           | 7                    | 23.65                                                        |
| 13         | Charlevoix-Est         | podzolic         | 2048                         | 7           |                      |                                                              |
|            |                        | rockland         | 510                          | 8           | 7                    | 2.56                                                         |



Québec (Cont'd)

|    |                     |                                     |                      |                 |     |       |
|----|---------------------|-------------------------------------|----------------------|-----------------|-----|-------|
| 14 | Charlevoix-Ouest    | podzolic<br>rockland                | 2030<br>1945         | 7<br>8          | 7   | 3.98  |
| 15 | Châteauguay         | brunsolic<br>gleysolic              | 520<br>104           | 6-7<br>5-6      | 6   | 6.24  |
| 16 | Chicoutimi          | podzolic<br>rockland                | 33995<br>5222        | 7<br>8          | 7   | 39.22 |
| 17 | Compton             | podzolic                            | 2048                 | 7               | 7   | 2.05  |
| 18 | Deux-montagnes      | brunisolic                          | 819                  | 6-7             | 6-7 | 4.10  |
| 19 | Dorchester          | podzolic                            | 2457                 | 7               | 7   | 2.56  |
| 20 | Drummond            | podzolic                            | 1434                 | 7               | 7   | 1.43  |
| 21 | Frontenac           | podzolic                            | 3379                 | 7               | 7   | 3.38  |
| 22 | Gaspé-Est           | podzolic<br>brunisolic              | 2560<br>4403         | 7<br>6-7        | 6-7 | 34.82 |
| 23 | Gaspé-Ouest         | podzolic                            | 5939                 | 7               | 7   | 5.94  |
| 24 | Gatineau            | podzolic<br>brunisolic<br>gleysolic | 1331<br>1024<br>3175 | 7<br>6-7<br>5-6 | 5-6 | 216.5 |
| 25 | Hull                | gleysolic                           | 409                  | 5-6             | 5-6 | 20.5  |
| 26 | Huntingdon          | podzolic<br>gleysolic               | 405<br>614           | 7<br>5-6        | 5-6 | 50.9  |
| 27 | Iberville           | brunisolic                          | 512                  | 6-7             | 6-7 | 2.56  |
| 28 | Île-de-Montreal     | brunisolic                          | 307                  | 6-7             | 6-7 | 1.55  |
| 29 | Île-de-la-Madeleine | brunisolic                          | 200                  | 6-7             | 6-7 | 1.00  |

Québec (Cont'd)

|    |                         |            |       |     |     |       |
|----|-------------------------|------------|-------|-----|-----|-------|
| 30 | Joliette                | podzolic   | 6143  | 7   |     |       |
|    |                         | gleysolic  | 306   | 5-6 |     |       |
|    |                         | brunisolic | 205   | 6-7 |     |       |
|    |                         |            |       |     | 6   | 66.50 |
| 31 | Kamouraska              | podzolic   | 2969  | 7   |     |       |
|    |                         |            |       |     | 7   | 2.97  |
| 32 | Labelle                 | podzolic   | 5765  | 7   |     |       |
|    |                         | brunisolic | 3482  | 6-7 |     |       |
|    |                         | gleysolic  | 717   | 5-6 |     |       |
|    |                         |            |       |     | 6   | 99.64 |
| 33 | Lac St. Jean -<br>Est   | podzolic   | 2252  | 7   |     |       |
|    |                         | gleysolic  | 922   | 5-6 |     |       |
|    |                         |            |       |     | 6   | 31.74 |
| 34 | Lac St. Jean -<br>Ouest | podzolic   | 54577 | 7   |     |       |
|    |                         | gleysolic  | 717   | 5-6 |     |       |
|    |                         | rockland   | 2253  | 8   |     |       |
|    |                         |            |       |     | 7   | 64.10 |
| 35 | La Prairie              | gleysolic  | 409   | 5-6 |     |       |
|    |                         |            |       |     | 5-6 | 20.45 |
| 36 | L'Assumption            | podzolic   | 307   | 7   |     |       |
|    |                         | brunisolic | 410   | 6-7 |     |       |
|    |                         |            |       |     | 6-7 | 3.59  |
| 37 | Lèvis                   | podzolic   | 409   | 7   |     |       |
|    |                         |            |       |     | 7   | 0.41  |
| 38 | L'Islet                 | podzolic   | 2252  | 7   |     |       |
|    |                         |            |       |     | 7   | 2.25  |
| 39 | L'Atbinière             | podzolic   | 1843  | 7   |     |       |
|    |                         |            |       |     | 7   | 1.84  |
| 40 | Maskinongé              | podzolic   | 5836  | 7   |     |       |
|    |                         | gleysolic  | 307   | 5-6 |     |       |
|    |                         |            |       |     | 6-7 | 30.70 |
| 41 | Montane                 | podzolic   | 4607  | 7   |     |       |
|    |                         |            |       |     | 7   | 4.61  |
| 42 | Matapédia               | podzolic   | 3582  | 7   |     |       |
|    |                         |            |       |     | 7   | 3.58  |
| 43 | Mégantic                | podzolic   | 1945  | 7   |     |       |
|    |                         |            |       |     | 7   | 1.95  |
| 44 | Missisquoi              | podzolic   | 102   | 7   |     |       |
|    |                         | luvisolic  | 103   | 7   |     |       |
|    |                         | brunisolic | 818   | 6-7 |     |       |
|    |                         |            |       |     | 6-7 | 5.12  |



Québec (Cont'd)

|    |                 |             |       |     |     |        |
|----|-----------------|-------------|-------|-----|-----|--------|
| 45 | Montcalm        | podzolic    | 5409  | 7   |     |        |
|    |                 | brunisollic | 1024  | 6-7 |     |        |
|    |                 | gleysolic   | 512   | 5-6 |     |        |
|    |                 |             |       |     | 6   | 69.40  |
| 46 | Montmagny       | podzolic    | 1739  | 7   |     |        |
|    |                 |             |       |     | 7   | 1.74   |
| 47 | Montmorency 1   | podzolic    | 3891  | 7   |     |        |
|    |                 | rockland    | 1741  | 8   |     |        |
|    |                 |             |       |     | 7   | 5.63   |
| 48 | Montmorency 2   | podzolic    | 189   | 7   |     |        |
|    |                 |             |       |     | 7   | 0.19   |
| 49 | Napierville     | brunisollic | 102   | 6-7 |     |        |
|    |                 | gleysolic   | 205   | 5-6 |     |        |
|    |                 |             |       |     | 5-6 | 15.35  |
| 0  | Nicolet         | podzolic    | 1433  | 7   |     |        |
|    |                 |             |       |     | 7   | 1.43   |
| 51 | Papineau        | brunisollic | 2253  | 6-7 |     |        |
|    |                 | gleysolic   | 1843  | 5-6 |     |        |
|    |                 |             |       |     | 5-6 | 204.80 |
| 52 | Pontiac         | brunisollic | 3354  | 6-7 |     |        |
|    |                 | gleysolic   | 2236  | 5-6 |     |        |
|    |                 | podzolic    | 19620 | 7   |     |        |
|    |                 |             |       |     | 6-7 | 126.10 |
| 53 | Portneuf        | podzolic    | 4095  | 7   |     |        |
|    |                 |             |       |     | 7   | 4.10   |
| 54 | Québec          | podzolic    | 6040  | 7   |     |        |
|    |                 | rockland    | 819   | 8   |     |        |
|    |                 |             |       |     | 7   | 6.86   |
| 55 | Richelieu       | podzolic    | 358   | 7   |     |        |
|    |                 | gleysolic   | 51    | 5-6 |     |        |
|    |                 |             |       |     | 6-7 | 2.05   |
| 56 | Richmond        | podzolic    | 1433  | 7   |     |        |
|    |                 |             |       |     | 7   | 1.43   |
| 57 | Rimouski        | podzolic    | 5734  | 7   |     |        |
|    |                 |             |       |     | 7   | 5.73   |
| 58 | Rivière du Loup | podzolic    | 3481  | 7   |     |        |
|    |                 |             |       |     | 7   | 3.48   |
| 59 | Rouville        | brunisollic | 409   | 6-7 |     |        |
|    |                 | gleysolic   | 205   | 5-6 |     |        |
|    |                 |             |       |     | 6   | 6.14   |

Québec (Cont'd)

|    |               |             |        |     |     |        |
|----|---------------|-------------|--------|-----|-----|--------|
| 60 | Saguenay      | brunisollic | 4914   | 6-7 |     |        |
|    |               | podzolic    | 187698 | 7   |     |        |
|    |               | rockland    | 20462  | 8   |     |        |
|    |               |             |        |     | 7   | 216.70 |
| 61 | St. Hyacinthe | podzolic    | 102    | 7   |     |        |
|    |               | brunisollic | 205    | 6-7 |     |        |
|    |               | gleysolic   | 409    | 5-6 |     |        |
|    |               |             |        |     | 5-6 | 35.80  |
| 62 | St. Jean      | brunisollic | 409    | 6-7 |     |        |
|    |               |             |        |     | 6-7 | 2.05   |
| 63 | St. Maurice   | podzolic    | 4709   | 7   |     |        |
|    |               |             | 307    | 5-6 |     |        |
|    |               |             |        |     | 6-7 | 25.10  |
| 64 | Shefford      | podzolic    | 1228   | 7   |     |        |
|    |               | brunisollic | 308    | 6-7 |     |        |
|    |               |             |        |     | 7   | 1.53   |
| 65 | Sherbrooke    | brunisollic | 614    | 6-7 |     |        |
|    |               | gleysolic   | 103    | 5-6 |     |        |
|    |               |             |        |     | 6-7 | 3.56   |
| 66 | Soulanger     | gleysolic   | 346    | 5-6 |     |        |
|    |               |             |        |     | 5-6 | 17.30  |
| 67 | Stanstead     | podzolic    | 1228   | 7   |     |        |
|    |               |             |        |     | 7   | 1.23   |
| 68 | Témiscamingue | podzolic    | 22654  | 7   |     |        |
|    |               | luvisolic   | 1530   | 7   |     |        |
|    |               |             |        |     | 7   | 24.18  |
| 69 | Témisconata   | podzolic    | 1941   | 7   |     |        |
|    |               |             |        |     | 7   | 1.94   |
| 70 | Terrebonne    | podzolic    | 409    | 7   |     |        |
|    |               | brunisollic | 2047   | 6-7 |     |        |
|    |               |             |        |     | 6-7 | 12.28  |
| 71 | Vaudrouil     | brunisollic | 511    | 6-7 |     |        |
|    |               |             |        |     | 6-7 | 2.56   |
| 72 | Verchères     | podzolic    | 307    | 7   |     |        |
|    |               | gleysolic   | 205    | 5-6 |     |        |
|    |               |             |        |     | 6   | 5.12   |
| 73 | Wolfe         | podzolic    | 920    | 7   |     |        |
|    |               |             |        |     | 7   | 0.92   |
| 74 | Yamaska       | podzolic    | 921    | 7   |     |        |
|    |               |             |        |     | 7   | 0.92   |



Québec (Cont'd)

|                |                |           |        |   |     |        |
|----------------|----------------|-----------|--------|---|-----|--------|
| A              | Abitibi        | podzolic  | 39320  | 7 | 6-7 | 259.40 |
|                |                | luvisolic | 1617   | 7 |     |        |
|                |                | organic   | 10940  | 6 |     |        |
| B              | Mistassini     | podzolic  | 56519  | 7 | 6-7 | 372.20 |
|                |                | organic   | 17516  | 6 |     |        |
|                |                | rockland  | 409    | 8 |     |        |
|                |                |           |        |   |     |        |
| C              | Nouveau-Québec | podzolic  | 156669 | 8 | 8-9 | 35.90  |
|                |                | organic   | 50073  | 7 |     |        |
|                |                | rockland  | 511276 | 9 |     |        |
|                |                |           |        |   |     |        |
| Québec - Total |                |           |        |   |     | 2340.0 |

# COUNTY RANKING AND SULPHUR PRODUCTIVITY

| <u>Ontario</u> |                            |                  |                                  |             |                          | Sulphur<br>Production<br>(10 <sup>7</sup> g yr <sup>-1</sup> ) |
|----------------|----------------------------|------------------|----------------------------------|-------------|--------------------------|----------------------------------------------------------------|
| <u>No.</u>     | <u>Census<br/>Division</u> | <u>Soil Type</u> | <u>Area<br/>(Km<sup>2</sup>)</u> | <u>Rank</u> | <u>Division<br/>Rank</u> |                                                                |
| 1              | Algoma                     | podzolic         | 50586                            | 7           | 7                        | 80.60                                                          |
|                |                            | brunisollic      | 2969                             | 6-7         |                          |                                                                |
|                |                            | rockland         | 307                              | 8           |                          |                                                                |
| 2              | Brant                      | brunisollic      | 9369                             | 6-7         | 6-7                      | 46.90                                                          |
| 3              | Bruce                      | podzolic         | 1843                             | 7           | 6-7                      | 23.30                                                          |
|                |                            | brunisollic      | 2815                             | 6-7         |                          |                                                                |
| 4              | Cochrane                   | luvisolic        | 16891                            | 7           | 6                        | 1433.00                                                        |
|                |                            | podzolic         | 23039                            | 7           |                          |                                                                |
|                |                            | gleysolic        | 29490                            | 5-6         |                          |                                                                |
|                |                            | organic          | 73931                            | 6           |                          |                                                                |
| 5              | Dufferin                   | luvisolic        | 1380                             | 7           | 7                        | 1.47                                                           |
|                |                            | brunisollic      | 92                               | 7           |                          |                                                                |
| 6              | Dundas                     | podzolic         | 51                               | 7           | 5-6                      | 43.50                                                          |
|                |                            | brunisollic      | 205                              | 6-7         |                          |                                                                |
|                |                            | gleysolic        | 614                              | 5-6         |                          |                                                                |
| 7              | Durham                     | luvisolic        | 1639                             | 7           | 7                        | 1.64                                                           |
| 8              | Elgin                      | luvisolic        | 2355                             | 7           | 7                        | 2.41                                                           |
|                |                            | gleysolic        | 51                               | 5-6         |                          |                                                                |
| 9              | Essex                      | luvisolic        | 205                              | 7           | 7                        | 0.21                                                           |
| 10             | Frontenac                  | luvisolic        | 717                              | 7           | 6-7                      | 13.30                                                          |
|                |                            | podzolic         | 309                              | 7           |                          |                                                                |
|                |                            | brunisollic      | 1639                             | 6-7         |                          |                                                                |
| 11             | Glengarry                  | brunisollic      | 870                              | 6-7         | 5-6                      | 54.00                                                          |
|                |                            | gleysolic        | 205                              | 5-6         |                          |                                                                |



Ontario (Cont'd)

|    |                       |                                                           |                                             |                         |     |         |
|----|-----------------------|-----------------------------------------------------------|---------------------------------------------|-------------------------|-----|---------|
| 12 | Grenville             | brunisolc<br>gleysolic                                    | 259<br>409                                  | 6-7<br>5-6              | 5-6 | 33.90   |
| 13 | Grey                  | podzolic<br>brunisolc                                     | 2967<br>2046                                | 7<br>6-7                | 7   | 5.01    |
| 14 | Haldimand             | luvisolic                                                 | 1230                                        | 7                       | 7   | 1.23    |
| 15 | Haliburton            | podzolic                                                  | 4710                                        | 7                       | 7   | 4.71    |
| 16 | Halton                | luvisolic                                                 | 921                                         | 7                       | 7   | 0.92    |
| 17 | Hastings              | luvisolic<br>podzolic<br>brunisolc                        | 820<br>4403<br>1229                         | 7<br>7<br>6-7           | 7   | 6.45    |
| 18 | Huron                 | gleysolic<br>luvisolic                                    | 864<br>2500                                 | 5-6<br>7                | 6   | 33.64   |
| 19 | Kenora                | luvisolic<br>podzolic<br>gleysolic<br>organic<br>rockland | 41881<br>144076<br>29081<br>169983<br>11674 | 7<br>7<br>5-6<br>6<br>8 | 6   | 3967.50 |
| 20 | Kent                  | luvisolic<br>gleysolic                                    | 1024<br>1741                                | 7<br>5-6                | 5-6 | 138.00  |
| 21 | Lambton               | luvisolic<br>gleysolic                                    | 819<br>2048                                 | 7<br>5-6                | 5-6 | 143.00  |
| 22 | Lanark                | luvisolic<br>podzolic<br>brunisolc                        | 205<br>1024<br>1945                         | 7<br>7<br>6-7           | 7   | 3.20    |
| 23 | Leeds                 | luvisolic<br>podzolic<br>brunisolc                        | 614<br>803<br>920                           | 7<br>7<br>6-7           | 7   | 2.32    |
| 24 | Lennox &<br>Addington | luvisolic<br>podzolic<br>brunisolc                        | 614<br>819<br>912                           | 7<br>7<br>6-7           | 7   | 2.40    |

Ontario (Cont'd)

|    |                      |            |       |     |     |       |
|----|----------------------|------------|-------|-----|-----|-------|
| 25 | Manitoulin           | brunisolic | 4505  | 6-7 | 6-7 | 22.60 |
| 26 | Middlesex            | luvisolic  | 3276  | 7   |     |       |
|    |                      | gleysolic  | 102   | 5-6 | 7   | 3.38  |
| 27 | Muskoka              | podzolic   | 4300  | 7   | 7   | 4.30  |
| 28 | Niagara              | luvisolic  | 1228  | 7   |     |       |
|    |                      | gleysolic  | 819   | 5-6 | 6   | 20.47 |
| 29 | Nipissing            | podzolic   | 18022 | 7   |     |       |
|    |                      | gleysolic  | 614   | 5-6 | 6-7 | 93.20 |
| 30 | Norfolk              | luvisolic  | 1944  | 7   | 7   | 1.94  |
| 31 | Northumberland       | luvisolic  | 1945  | 7   | 7   | 1.94  |
| 32 | Ontario              | podzolic   | 102   | 7   |     |       |
|    |                      | luvisolic  | 1945  | 7   | 7   | 2.05  |
| 33 | Ottawa -<br>Carleton | brunisolic | 2149  | 6-7 |     |       |
|    |                      | luvisolic  | 1331  | 7   |     |       |
|    |                      | gleysolic  | 204   | 5-6 | 6-7 | 18.35 |
| 34 | Oxford               | luvisolic  | 2047  | 7   | 7   | 2.05  |
| 35 | Parry Sound          | rockland   | 1228  | 8   |     |       |
|    |                      | podzolic   | 9011  | 7   | 7   | 10.23 |
| 36 | Peel                 | luvisolic  | 1279  | 7   | 7   | 1.28  |
| 37 | Perth                | gleysolic  | 542   | 5-6 |     |       |
|    |                      | luvisolic  | 1624  | 7   | 6   | 21.66 |
| 38 | Peterborough         | podzolic   | 2048  | 7   |     |       |
|    |                      | brunisolic | 306   | 6-7 |     |       |
|    |                      | luvisolic  | 1433  | 7   | 7   | 3.78  |
| 39 | Prescott             | podzolic   | 102   | 7   |     |       |
|    |                      | brunisolic | 204   | 6-7 | 7   | 0.30  |



Ontario (Cont'd)

|    |               |             |        |     |     |        |
|----|---------------|-------------|--------|-----|-----|--------|
| 40 | Prince Edward | brunisollic | 1228   | 6-7 | 6-7 | 6.15   |
| 41 | Rainy River   | luvisolic   | 3481   | 7   |     |        |
|    |               | podzolic    | 15461  | 7   | 7   | 18.94  |
| 42 | Renfrew       | podzolic    | 512    | 7   | 7   | 0.51   |
| 43 | Russell       | podzolic    | 409    | 7   |     |        |
|    |               | brunisollic | 102    | 6-7 | 7   | 0.51   |
| 44 | Simcoe        | luvisolic   | 2968   | 7   |     |        |
|    |               | podzolic    | 521    | 7   |     |        |
|    |               | brunisollic | 204    | 6-7 | 7   | 3.72   |
| 45 | Stormont      | podzolic    | 51     | 7   |     |        |
|    |               | brunisollic | 512    | 6-7 |     |        |
|    |               | gleysolic   | 204    | 5-6 | 6   | 7.67   |
| 46 | Sudbury       | podzolic    | 39936  | 7   |     |        |
|    |               | brunisollic | 4915   | 6-7 |     |        |
|    |               | gleysolic   | 1331   | 5-6 |     |        |
|    |               | rockland    | 1228   | 8   | 6-7 | 236.90 |
| 47 | Thunder Bay   | luvisolic   | 6040   | 7   |     |        |
|    |               | podzolic    | 102806 | 7   |     |        |
|    |               | brunisollic | 819    | 6-7 |     |        |
|    |               | rockland    | 1945   | 8   | 7   | 111.60 |
| 48 | Timiskaming   | luvisolic   | 2457   | 7   |     |        |
|    |               | podzolic    | 14028  | 7   | 7   | 16.48  |
| 49 | Toronto       | luvisolic   | 620    | 7   | 7   | 0.62   |
| 50 | Victoria      | luvisolic   | 2251   | 7   |     |        |
|    |               | brunisollic | 819    | 6-7 | 7   | 3.07   |
| 51 | Waterloo      | luvisolic   | 1313   | 7   | 7   | 1.31   |
| 52 | Wellington    | luvisolic   | 2627   | 7   | 7   | 2.63   |

Ontario (Cont'd)

|    |           |           |      |   |   |      |
|----|-----------|-----------|------|---|---|------|
| 53 | Wentworth | luvisolic | 1177 | 7 | 7 | 1.18 |
| 54 | York      | luvisolic | 1735 | 7 | 7 | 1.74 |

Ontario - Total 6594.4



# COUNTY RANKING AND SULPHUR PRODUCTION

## Manitoba

| <u>Census<br/>Division</u> | <u>Soil Type</u> | <u>Area (km<sup>2</sup>)</u> | <u>Rank</u> | <u>Division<br/>Rank</u> | <u>Sulphur<br/>Production<br/>(10<sup>7</sup> g yr<sup>-1</sup>)</u> |
|----------------------------|------------------|------------------------------|-------------|--------------------------|----------------------------------------------------------------------|
| Division 1                 | chernozemic      | 2559                         | 6-7         |                          |                                                                      |
|                            | luvisolic        | 409                          | 7           |                          |                                                                      |
|                            | regosolic        | 307                          | 7           |                          |                                                                      |
|                            | gleysolic        | 716                          | 5-6         |                          |                                                                      |
|                            | organic          | 204                          | 6           | 6                        | 41.90                                                                |
| Division 2                 | chernozemic      | 4709                         | 6-7         |                          |                                                                      |
|                            | gleysolic        | 921                          | 5-6         | 6                        | 56.30                                                                |
| Division 3                 | chernozemic      | 6449                         | 6-7         | 6-7                      | 32.30                                                                |
| Division 4                 | chernozemic      | 6143                         | 6-7         | 6-7                      | 30.70                                                                |
| Division 5                 | chernozemic      | 1145                         | 6-7         |                          |                                                                      |
|                            | luvisolic        | 307                          | 7           | 6-7                      | 7.40                                                                 |
| Division 6                 | chernozemic      | 6347                         | 6-7         | 6-7                      | 31.80                                                                |
|                            |                  |                              |             |                          |                                                                      |
| Division 7                 | chernozemic      | 5731                         | 6-7         | 6-7                      | 28.65                                                                |
|                            |                  |                              |             |                          |                                                                      |
| Division 8                 | chernozemic      | 5323                         | 6-7         | 6-7                      | 26.60                                                                |
|                            |                  |                              |             |                          |                                                                      |
| Division 9                 | chernozemic      | 3071                         | 6-7         | 6-7                      | 15.35                                                                |
|                            |                  |                              |             |                          |                                                                      |
| Division 10                | chernozemic      | 4402                         | 6-7         |                          |                                                                      |
|                            | luvisolic        | 716                          | 7           | 6-7                      | 25.60                                                                |
| Division 11                | chernozemic      | 3276                         | 6-7         |                          |                                                                      |
|                            | luvisolic        | 3993                         | 7           | 7                        | 7.30                                                                 |
| Division 12                | chernozemic      | 11058                        | 7           |                          |                                                                      |
|                            | luvisolic        | 11161                        | 6-7         | 7                        | 22.20                                                                |

Manitoba (Cont'd)

|                  |             |        |     |     |         |
|------------------|-------------|--------|-----|-----|---------|
| Division 13      | chernozemic | 4812   | 6-7 |     |         |
|                  | luvisolic   | 102    | 7   |     |         |
|                  |             |        |     | 6-7 | 24.60   |
| Division 14      | chernozemic | 1125   | 6-7 |     |         |
|                  | luvisolic   | 920    | 7   |     |         |
|                  |             |        |     | 6-7 | 10.30   |
| Division 15      | chernozemic | 3685   | 6-7 |     |         |
|                  | luvisolic   | 4670   | 7   |     |         |
|                  | organic     | 716    | 7   |     |         |
|                  |             |        |     | 7   | 9.07    |
| Division 16      | chernozemic | 2048   | 6-7 |     |         |
|                  | luvisolic   | 76798  | 7   |     |         |
|                  | podzolic    | 122162 | 7   |     |         |
|                  | brunisolc   | 7884   | 6-7 |     |         |
|                  | gleysolic   | 2662   | 5-6 |     |         |
|                  | organic     | 178480 | 6   |     |         |
|                  | rockland    | 4300   | 8   |     |         |
|                  |             |        |     | 6-7 | 1971.50 |
| Division 17      | chernozemic | 4812   | 6-7 |     |         |
|                  | luvisolic   | 153    | 7   |     |         |
|                  |             |        |     | 6-7 | 24.80   |
| Division 18      | chernozemic | 8192   | 6-7 |     |         |
|                  | organic     | 102    | 6   |     |         |
|                  |             |        |     | 6-7 | 41.40   |
| Division 19      | chernozemic | 2046   | 6-7 |     |         |
|                  | luvisolic   | 102    | 7   |     |         |
|                  | regosolic   | 2456   | 7   |     |         |
|                  | gleysolic   | 819    | 5-6 |     |         |
|                  | organic     | 13413  | 6   |     |         |
|                  | rockland    | 4915   | 8   |     |         |
|                  |             |        |     | 6   | 2375.00 |
| Division 20      | chernozemic | 614    | 6-7 |     |         |
|                  |             |        |     | 6-7 | 3.07    |
| Manitoba - Total |             |        |     |     | 4786.0  |



# COUNTY RANKING AND SULPHUR PRODUCTION

## Saskatchewan

| <u>Census<br/>Division</u> | <u>Soil Type</u> | <u>Area (km<sup>2</sup>)</u> | <u>Rank</u> | <u>Division<br/>Rank</u> | <u>Sulphur<br/>Production<br/>(10<sup>7</sup> g yr<sup>-1</sup>)</u> |
|----------------------------|------------------|------------------------------|-------------|--------------------------|----------------------------------------------------------------------|
| Division 1                 | chernozemic      | 13412                        | 6-7         |                          |                                                                      |
|                            | solonetzic       | 102                          | 6           | 6-7                      | 67.60                                                                |
| Division 2                 | chernozemic      | 9726                         | 6-7         |                          |                                                                      |
|                            | solonetzic       | 6348                         | 6           |                          |                                                                      |
|                            | gleysolic        | 819                          | 5-6         | 6                        | 84.50                                                                |
| Division 3                 | chernozemic      | 19041                        | 6-7         |                          |                                                                      |
|                            | regosolic        | 102                          | 7           |                          |                                                                      |
|                            | gleysolic        | 102                          | 5-6         | 6-7                      | 96.30                                                                |
| Division 4                 | chernozemic      | 16893                        | 6-7         |                          |                                                                      |
|                            | solonetzic       | 2047                         | 6           | 6-7                      | 94.70                                                                |
| Division 5                 | chernozemic      | 14639                        | 6-7         |                          |                                                                      |
|                            |                  |                              |             | 6-7                      | 73.20                                                                |
| Division 6                 | chernozemic      | 16380                        | 6-7         |                          |                                                                      |
|                            | gleysolic        | 102                          | 5-6         | 6-7                      | 82.40                                                                |
| Division 7                 | chernozemic      | 14640                        | 6-7         |                          |                                                                      |
|                            | solonetzic       | 716                          | 6           |                          |                                                                      |
|                            | regosolic        | 1945                         | 7           |                          |                                                                      |
|                            | gleysolic        | 409                          | 5-6         | 6-7                      | 88.60                                                                |
| Division 8                 | chernozemic      | 16736                        | 6-7         |                          |                                                                      |
|                            | regosolic        | 1023                         | 7           | 6-7                      | 88.80                                                                |
| Division 9                 | chernozemic      | 9008                         | 6-7         |                          |                                                                      |
|                            | luvisolic        | 3481                         | 7           | 6-7                      | 62.25                                                                |
| Division 10                | chernozemic      | 10648                        | 6-7         |                          |                                                                      |
|                            | luvisolic        | 2252                         | 7           |                          |                                                                      |
|                            | regosolic        | 819                          | 7           | 6-7                      | 68.60                                                                |
| Division 11                | chernozemic      | 19350                        | 6-7         |                          |                                                                      |
|                            | solonetzic       | 1126                         | 6           |                          |                                                                      |
|                            | regosolic        | 2150                         | 7           | 6-7                      | 113.20                                                               |

Saskatchewan (Cont'd)

|             |             |        |     |     |        |
|-------------|-------------|--------|-----|-----|--------|
| Division 12 | chernozemic | 12592  | 6-7 |     |        |
|             | regosolic   | 1228   | 7   |     |        |
|             |             |        |     | 6-7 | 69.20  |
| Division 13 | chernozemic | 12996  | 6-7 |     |        |
|             | solonetzic  | 1740   | 6   |     |        |
|             | regosolic   | 1331   | 7   |     |        |
|             |             |        |     | 6-7 | 80.40  |
| Division 14 | chernozemic | 10649  | 6-7 |     |        |
|             | luvisolic   | 15663  | 7   |     |        |
|             | organic     | 6553   | 6   |     |        |
|             |             |        |     | 6-7 | 164.40 |
| Division 15 | chernozemic | 9418   | 6-7 |     |        |
|             | luvisolic   | 8188   | 7   |     |        |
|             | regosolic   | 2355   | 7   |     |        |
|             |             |        |     | 6-7 | 99.50  |
| Division 16 | chernozemic | 8293   | 6-7 |     |        |
|             | luvisolic   | 11467  | 7   |     |        |
|             | regosolic   | 614    | 7   |     |        |
|             | organic     | 102    | 6   |     |        |
|             |             |        |     | 7   | 20.50  |
| Division 17 | chernozemic | 6959   | 6-7 |     |        |
|             | luvisolic   | 13002  | 7   |     |        |
|             |             |        |     | 7   | 19.96  |
| Division 18 | chernozemic | 409    | 6-7 |     |        |
|             | luvisolic   | 40444  | 7   |     |        |
|             | podzolic    | 198857 | 7   |     |        |
|             | organic     | 19761  | 6   |     |        |
|             | rockland    | 3584   | 8   |     |        |
|             |             |        |     | 7   | 263.06 |

Saskatchewan - Total      1637.3



# COUNTY RANKING AND SULPHUR PRODUCTION

## Alberta

| <u>Census<br/>Division</u> | <u>Soil Type</u> | <u>Area (km<sup>2</sup>)</u> | <u>Rank</u> | <u>Division<br/>Rank</u> | <u>Sulphur<br/>Production<br/>(10<sup>7</sup> g yr<sup>-1</sup>)</u> |
|----------------------------|------------------|------------------------------|-------------|--------------------------|----------------------------------------------------------------------|
| Division 1                 | chernozemic      | 18227                        | 6-7         |                          |                                                                      |
|                            | solonetzic       | 2662                         | 6           |                          |                                                                      |
|                            | regosolic        | 409                          | 7           | 6-7                      | 106.50                                                               |
| Division 2                 | chernozemic      | 17920                        | 6-7         |                          |                                                                      |
|                            | solonetzic       | 3788                         | 6           | 6-7                      | 108.60                                                               |
| Division 3                 | chernozemic      | 13414                        | 6-7         |                          |                                                                      |
|                            | rockland         | 307                          | 8           | 6-7                      | 68.60                                                                |
| Division 4                 | chernozemic      | 19968                        | 6-7         |                          |                                                                      |
|                            | solonetzic       | 11468                        | 6           |                          |                                                                      |
|                            | regosolic        | 307                          | 7           | 6                        | 317.40                                                               |
| Division 5                 | chernozemic      | 15564                        | 6-7         |                          |                                                                      |
|                            | solonetzic       | 512                          | 6           | 6-7                      | 80.40                                                                |
| Division 6                 | chernozemic      | 12492                        | 6-7         |                          |                                                                      |
|                            | luvisolic        | 1433                         | 7           | 6-7                      | 69.70                                                                |
| Division 7                 | chernozemic      | 13619                        | 6-7         |                          |                                                                      |
|                            | solonetzic       | 6426                         | 6           |                          |                                                                      |
|                            | regosolic        | 102                          | 7           | 6                        | 99.90                                                                |
| Division 8                 | chernozemic      | 5836                         | 6-7         |                          |                                                                      |
|                            | luvisolic        | 6656                         | 7           | 6-7                      | 62.50                                                                |
| Division 9                 | chernozemic      | 1740                         | 6-7         |                          |                                                                      |
|                            | luvisolic        | 13516                        | 7           |                          |                                                                      |
|                            | organic          | 1536                         | 6           |                          |                                                                      |
|                            | rockland         | 27340                        | 8           | 7                        | 220.70                                                               |
| Division 10                | chernozemic      | 13516                        | 6-7         |                          |                                                                      |
|                            | solonetzic       | 4505                         | 6           |                          |                                                                      |
|                            | luvisolic        | 1433                         | 7           | 6-7                      | 97.25                                                                |

Alberta (Cont'd)

|                 |             |       |     |     |         |
|-----------------|-------------|-------|-----|-----|---------|
| Division 11     | chernozemic | 5120  | 6-7 |     |         |
|                 | solonetzic  | 102   | 6   |     |         |
|                 | luvisolic   | 5939  | 7   |     |         |
|                 | organic     | 307   | 6   | 6-7 | 57.40   |
| Division 12     | chernozemic | 1638  | 6-7 |     |         |
|                 | luvisolic   | 35737 | 7   |     |         |
|                 | podzolic    | 9113  | 7   |     |         |
|                 | brunisollic | 3891  | 6-7 |     |         |
|                 | regosolic   | 4710  | 7   |     |         |
|                 | gleysolic   | 8908  | 5-6 |     |         |
|                 | organic     | 53862 | 6   |     |         |
|                 | rockland    | 9318  | 8   | 6-7 | 636.00  |
| Division 13     | chernozemic | 819   | 6-7 |     |         |
|                 | solonetzic  | 1024  | 6   |     |         |
|                 | luvisolic   | 17408 | 7   |     |         |
|                 | gleysolic   | 1536  | 5-6 |     |         |
|                 | organic     | 2662  | 6   | 6-7 | 117.30  |
| Division 14     | luvisolic   | 21401 | 7   |     |         |
|                 | organic     | 5222  | 6   |     |         |
|                 | rockland    | 5120  | 8   | 7   | 31.70   |
| Division 15     | solonetzic  | 35430 | 6   |     |         |
|                 | luvisolic   | 94412 | 7   |     |         |
|                 | podzolic    | 512   | 7   |     |         |
|                 | brunisollic | 7270  | 6-7 |     |         |
|                 | regosolic   | 7372  | 7   |     |         |
|                 | gleysolic   | 17920 | 5-6 |     |         |
|                 | organic     | 55398 | 6   |     |         |
|                 | rockland    | 3481  | 8   | 6-7 | 1109.00 |
| Alberta - Total |             |       |     |     | 3183.0  |



# COUNTY RANKING AND SULPHUR PRODUCTION

## British Columbia

| No. | Census Division       | Soil Type   | Area (km <sup>2</sup> ) | Rank | Division Rank | Sulphur Production (10 <sup>7</sup> g yr <sup>-1</sup> ) |
|-----|-----------------------|-------------|-------------------------|------|---------------|----------------------------------------------------------|
| 1   | Alberni - Clayoquat   | podzolic    | 5714                    | 7    |               |                                                          |
|     |                       | rockland    | 1935                    | 8    | 7             | 7.65                                                     |
| 2   | Bulkley - Nechaka     | luvisolic   | 55171                   | 7    |               |                                                          |
|     |                       | brunisollic | 7663                    | 6-7  |               |                                                          |
|     |                       | rockland    | 8428                    | 8    | 7             | 71.26                                                    |
| 3   | Capital               | podzolic    | 1100                    | 7    |               |                                                          |
|     |                       | brunisollic | 1191                    | 6-7  | 6-7           | 22.91                                                    |
| 4   | Cariboo               | chernozemic | 6223                    | 7    |               |                                                          |
|     |                       | luvisolic   | 35236                   | 7    |               |                                                          |
|     |                       | podzolic    | 8146                    | 7    |               |                                                          |
|     |                       | brunisollic | 7788                    | 6-7  |               |                                                          |
|     |                       | ice         | 732                     |      |               |                                                          |
|     |                       | rockland    | 10051                   | 8    | 7             | 68.37                                                    |
| 5   | Central Fraser Valley | gleysolic   | 699                     | 5-6  | 5-6           | 34.95                                                    |
| 6   | Central Kootenay      | podzolic    | 14738                   | 7    |               |                                                          |
|     |                       | brunisollic | 3254                    | 6-7  |               |                                                          |
|     |                       | gleysolic   | 479                     | 5-6  |               |                                                          |
|     |                       | ice         | 103                     |      |               |                                                          |
|     |                       | rockland    | 2871                    | 8    | 6-7           | 114.84                                                   |
| 7   | Central Okanagan      | chernozemic | 1317                    | 6    |               |                                                          |
|     |                       | luvisolic   | 1627                    | 7    |               |                                                          |
|     |                       | brunisollic | 155                     | 6-7  | 6-7           | 14.72                                                    |
| 8   | Columbia-Shuswap      | podzolic    | 10136                   | 7    |               |                                                          |
|     |                       | luvisolic   | 965                     | 7    |               |                                                          |
|     |                       | brunisollic | 1930                    | 6-7  |               |                                                          |
|     |                       | gleysolic   | 1448                    | 5-6  |               |                                                          |
|     |                       | ice         | 3668                    |      |               |                                                          |
|     |                       | rockland    | 16605                   | 8    | 6-7           | 149.16                                                   |

British Columbia (Cont'd)

|    |                       |                                                               |                                        |                           |     |        |
|----|-----------------------|---------------------------------------------------------------|----------------------------------------|---------------------------|-----|--------|
| 9  | Camax-<br>Strathcona  | podzolic<br>ice<br>rockland                                   | 7828<br>9899<br>1841                   | 7<br><br>8                | 7-8 | 9.90   |
| 10 | Cowichan-Valley       | podzolic<br>brunisollic                                       | 1970<br>1371                           | 7<br>6-7                  | 7   | 3.34   |
| 11 | Dewdney-Alouette      | podzolic<br>brunisollic<br>gleysolic<br>rockland              | 1464<br>955<br>127<br>573              | 7<br>6-7<br>5-6<br>8      | 6-7 | 15.59  |
| 12 | East Kootenay         | luvisolic<br>podzolic<br>brunisollic<br>gleysolic<br>rockland | 5627<br>1172<br>12191<br>1993<br>7033  | 7<br>7<br>6-7<br>5-6<br>8 | 6-7 | 140.08 |
| 13 | Fraser Cheam          | luvisolic<br>podzolic<br>brunisollic<br>gleysolic<br>rockland | 353<br>4938<br>4497<br>176<br>705      | 7<br>7<br>6-7<br>5-6<br>8 | 6-7 | 53.35  |
| 14 | Fraser Fort<br>George | luvisolic<br>podzolic<br>rockland<br>ice                      | 15437<br>10934<br>18653<br>459         | 7<br>7<br>8               | 7-8 | 22.74  |
| 15 | Greater Vancouver     | podzolic<br>brunisollic                                       | 361<br>1771                            | 7<br>6-7                  | 6-7 | 10.66  |
| 16 | Kitimat-Stikine       | luvisolic<br>podzolic<br>brunisollic<br>rockland<br>ice       | 524<br>45458<br>12255<br>31003<br>5447 | 7<br>7<br>6-7<br>8        | 7   | 94.69  |
| 17 | Kootenay<br>Boundary  | chernozemic<br>luvisolic<br>podzolic<br>brunisollic           | 1224<br>2354<br>1600<br>2637           | 6-7<br>7<br>7<br>6-7      | 6-7 | 39.08  |



British Columbia (Cont'd)

|    |                           |             |       |     |     |        |
|----|---------------------------|-------------|-------|-----|-----|--------|
| 18 | Mount Waddington          | podzolic    | 9005  | 7   | 7-8 | 10.61  |
|    |                           | rockland    | 3968  | 8   |     |        |
|    |                           | ice         | 2900  |     |     |        |
| 19 | Nanaimo                   | podzolic    | 924   | 7   | 6-7 | 10.09  |
|    |                           | brunisollic | 1093  | 6-7 |     |        |
| 20 | North Okanagan            | chernozemic | 837   | 6-7 | 7   | 7.74   |
|    |                           | luvisolic   | 1673  | 7   |     |        |
|    |                           | podzolic    | 5229  | 7   |     |        |
| 21 | Ocean Falls               | podzolic    | 10095 | 7   | 7   | 24.83  |
|    |                           | luvisolic   | 1009  | 7   |     |        |
|    |                           | brunisollic | 1211  | 6-7 |     |        |
|    |                           | rockland    | 9893  | 8   |     |        |
|    |                           | ice         | 2624  |     |     |        |
| 22 | Okanagan -<br>Similkameen | chernozemic | 3209  | 6-7 | 6-7 | 52.65  |
|    |                           | luvisolic   | 4011  | 7   |     |        |
|    |                           | brunisollic | 3309  | 6-7 |     |        |
| 23 | Peace River-<br>Liard     | solonetzic  | 1335  | 6   | 6-7 | 963.99 |
|    |                           | luvisolic   | 75496 | 7   |     |        |
|    |                           | brunisollic | 20646 | 6-7 |     |        |
|    |                           | regosolic   | 1643  | 7   |     |        |
|    |                           | organic     | 38005 | 6   |     |        |
|    |                           | rockland    | 55672 | 8   |     |        |
| 24 | Powell River              | podzolic    | 2219  | 7   | 7-8 | 2.52   |
|    |                           | rockland    | 1513  | 8   |     |        |
|    |                           | ice         | 1311  |     |     |        |
| 25 | Skeena                    | podzolic    | 15954 | 7   | 7   | 15.95  |
| 26 | Squamish-Lilloot          | chernozemic | 714   | 6-7 | 7   | 16.32  |
|    |                           | luvisolic   | 1020  | 7   |     |        |
|    |                           | podzolic    | 7548  | 7   |     |        |
|    |                           | brunisollic | 2754  | 6-7 |     |        |
|    |                           | rockland    | 2652  | 8   |     |        |
|    |                           | ice         | 1428  |     |     |        |

British Columbia (Cont'd)

|                          |                 |             |       |     |     |        |
|--------------------------|-----------------|-------------|-------|-----|-----|--------|
| 27                       | Stikine         | luvisolic   | 10138 | 7   |     |        |
|                          |                 | brunisollic | 37583 | 6-7 |     |        |
|                          |                 | rockland    | 55676 | 8   |     |        |
|                          |                 | ice         | 8478  |     |     |        |
|                          |                 |             |       |     | 6-7 | 559.39 |
| 28                       | Sunshine Coast  | podzolic    | 2321  | 7   |     |        |
|                          |                 | gleysolic   | 606   | 5-6 |     |        |
|                          |                 | rockland    | 908   | 8   |     |        |
|                          |                 |             |       |     | 6   | 38.35  |
| 29                       | Thompson-Nicola | chernozemic | 13057 | 6-7 |     |        |
|                          |                 | luvisolic   | 44373 | 7   |     |        |
|                          |                 | podzolic    | 9129  | 7   |     |        |
|                          |                 | brunisollic | 3609  | 6-7 |     |        |
|                          |                 | rockland    | 3715  | 8   |     |        |
|                          |                 | ice         | 530   |     |     |        |
|                          |                 |             |       |     | 6-7 | 221.86 |
| British Columbia - Total |                 |             |       |     |     | 2797.6 |



# COUNTY RANKING AND SULPHUR PRODUCTION

## Northwest Territories

|                               | <u>Soil Type</u> | <u>Area<br/>(km<sup>2</sup>)</u> | <u>Rank</u> | <u>Division<br/>Rank</u> | <u>Sulphur<br/>Production<br/>(kg x 10<sup>7</sup>g yr<sup>-1</sup>)</u> |
|-------------------------------|------------------|----------------------------------|-------------|--------------------------|--------------------------------------------------------------------------|
| District of MacKenzie         | luvisolic        | 102                              | 7           |                          |                                                                          |
|                               | podzolic         | 15360                            | 7           |                          |                                                                          |
|                               | brunisolc        | 87756                            | 6-7         |                          |                                                                          |
|                               | regosolic        | 105881                           | 7           |                          |                                                                          |
|                               | gleysolic        | 17817                            | 5-6         |                          |                                                                          |
|                               | organic          | 44339                            | 6           |                          |                                                                          |
|                               | rockland         | 5324                             | 8           |                          |                                                                          |
|                               |                  |                                  |             | 6-7                      | 1380.00                                                                  |
| District of Keewatin          | podzolic         | 1228                             | 7           |                          |                                                                          |
|                               | brunisolc        | 97792                            | 6-7         |                          |                                                                          |
|                               | regosolic        | 23347                            | 7           |                          |                                                                          |
|                               | rockland         | 1331                             | 8           | 6-7                      | 615.00                                                                   |
| District of Franklin          | regosolic        | 248729                           | 7           |                          |                                                                          |
|                               | rockland         | 33382                            | 8           |                          |                                                                          |
|                               |                  |                                  |             | 7                        | 282.10                                                                   |
| Northwest Territories - Total |                  |                                  |             |                          | 2277.10                                                                  |

# COUNTY RANKING AND SULPHUR PRODUCTION

## Yukon

| <u>Soil Type</u> | <u>Area (km<sup>2</sup>)</u> | <u>Rank</u> | <u>Division Rank</u> | <u>Sulphur Production<br/>(kg x 10<sup>7</sup>g yr<sup>-1</sup>)</u> |
|------------------|------------------------------|-------------|----------------------|----------------------------------------------------------------------|
| brunisollic      | 66764                        | 6-7         |                      |                                                                      |
| regosolic        | 10444                        | 7           |                      |                                                                      |
| gleysolic        | 3584                         | 5-6         |                      |                                                                      |
| rockland         | 18227                        | 8           |                      |                                                                      |

6-7 495.0

Yukon - Total 495.0



### 5.1.2 Vegetation

The estimated sulphur production by vegetation, summarized in Table 5-3, was obtained by applying the sulphur productivity rankings derived from consideration of soil climates (see Section 4.2.2). As an alternate, more detailed approach, a determination of sulphur production by typical vegetation occupying various soil temperatures is given in Table 5-4. The two estimates correspond quite closely - 8594 MT for the first estimate and 8918 MT for the second.

TABLE 5-3

## VEGETATION EMISSIONS

| <u>Vegetation</u>               | <u>Area<br/>(10<sup>6</sup>km<sup>2</sup>)</u> | <u>Ranking</u> | <u>Sulphur Production<br/>(metric tons as S)</u> |
|---------------------------------|------------------------------------------------|----------------|--------------------------------------------------|
| Tundra<br>Continuous permafrost | 2.76                                           | 10             | 28                                               |
| Tundra<br>Widespread permafrost | 2.36                                           | 9              | 236                                              |
| Open shrub forest               | 2.95                                           | 8              | 2,950                                            |
| Coniferous and mixed<br>forests | 0.949                                          | 7-8            | 4,750                                            |
| Deciduous forest                | 0.126                                          | 7-8            | 630                                              |
| Canada Total                    |                                                |                | 8,594                                            |



TABLE 5-4  
SULPHUR PRODUCTION BY VEGETATION  
( $10^6 \text{ gS yr}^{-1}$ )

|                                                         | ARCTIC & SUB-ARCTIC | CRYOBOREAL         | BOREAL             | MESIC     | TOTAL      |
|---------------------------------------------------------|---------------------|--------------------|--------------------|-----------|------------|
| Ranking                                                 | 9-10                | 8-9                | 7-8                | 8         |            |
| S Productivity<br>( $\text{gS m}^{-2} \text{ y}^{-1}$ ) | $5 \times 10^{-5}$  | $5 \times 10^{-4}$ | $5 \times 10^{-3}$ | $10^{-3}$ |            |
| Province                                                |                     |                    |                    |           |            |
| British Columbia                                        | 14.8                | 262.5              | 505                | --        | 795.3      |
| Alberta                                                 | 2.9                 | 213.5              | 800                | --        | 1016.4     |
| Saskatchewan                                            | 1.9                 | 158                | 1085               | --        | 1244.9     |
| Manitoba                                                | 8.3                 | 154                | 390                | --        | 552.3      |
| Ontario                                                 | 3.3                 | 134                | 2505               | 56        | 2698.3     |
| Quebec                                                  | 19.7                | 337.5              | 1410               | 5         | 1772.2     |
| New Brunswick                                           | --                  | 7.5                | 270                | --        | 277.5      |
| Nova Scotia                                             | --                  | 2                  | 220                | 4         | 226        |
| Newfoundland and<br>Labrador                            | 5.6                 | 132                | --                 | --        | 138.6      |
| Prince Edward Island                                    | --                  | --                 | 200                | --        | 200        |
|                                                         |                     |                    |                    |           | <hr/> 8918 |
|                                                         |                     |                    | Total Canada       |           |            |

(Determination by typical vegetation occupying various  
soil temperature climates)

### 5.1.3 Aquatic

The marine divisions presented in Table 5-5 are composed of the various marine classifications which were ranked for sulphur productivity in Section 4.2.3 (Table 4-5). An average sulphur ranking was derived for each division from the data of Owens (1977) which provided the relative frequency of each classification in the division. The emission rate corresponding to the sulphur ranking was then multiplied by the area and the ice-free period to obtain the estimates for coastal emissions of sulphur (see Table 5-6).

The estimated biogenic sulphur production from Canadian lakes is presented in Table 5-7.



TABLE 5-5

## SULPHUR EMISSION RANKING FOR COASTAL SHORELINE HABITATS

| <u>PACIFIC COAST (Figure 12)</u> |                              | <u>Sulphur<br/>Ranking</u> | <u>Ice Free<br/>Period</u> | <u>Classification</u> |
|----------------------------------|------------------------------|----------------------------|----------------------------|-----------------------|
| <u>Marine Divisions</u>          | <u>Area (km<sup>2</sup>)</u> |                            |                            |                       |
| 1                                | 1,044                        | 4                          | 1.0                        | III 11, IV 12         |
| 2                                | 10,962                       | 8                          | 1.0                        | I4, II5               |
| 3                                | 1,740                        | 8                          | 1.0                        | I2, II5               |
| 4                                | 72,732                       | 10                         | 1.0                        | I3                    |
| 5                                | 55,854                       | 10                         | 1.0                        | I2,                   |
| 6                                | 10,614                       | 8                          | 1.0                        | I4, II6               |

ARCTIC COAST (Figure 13)

|    |        |         |     |              |
|----|--------|---------|-----|--------------|
| 1  | 29,200 | 6 (8) * | 0.3 | II5, III10   |
| 2a | 36,400 | 6 (7)   | 0.2 | III 10       |
| 2b | 42,700 | 8 (9)   | 0.2 | I2, II 5     |
| 3  | 42,000 | 10 (-)  | 0.2 | I2, I3       |
| 4  | 12,400 | 10 (-)  | 0.2 | I3           |
| 5  | 10,000 | 10 (-)  | 0.1 | II, II5      |
| 6  | 3,600  | 10 (-)  | 0.0 | II, II5      |
| 7  | 34,400 | 10 (-)  | 0.1 | II, II5      |
| 8  | 11,600 | 9 (-)   | 0.1 | II, II5      |
| 9  | 60,000 | 9 (-)   | 0.2 | I2, II5      |
| 10 | 7,200  | 9 (-)   | 0.2 | II, II5, II6 |
| 11 | 4,400  | 5 (7)   | 0.2 | II6, IV12    |
| 12 | 3,200  | 8 (10)  | 0.2 | I4, II6      |

ATLANTIC COAST (Figure 8 & 9)

|   |        |    |     |               |
|---|--------|----|-----|---------------|
| 1 | 45,018 | 10 | 0.8 | II, II7       |
| 2 | 21,033 | 10 | 0.4 | II, II7       |
| 3 | 3,690  | 4  | 0.6 | III11, III 10 |
| 4 | 22,509 | 5  | 0.6 | II6, II7      |
| 5 | 11,439 | 8  | 0.9 | I2, II7       |
| 6 | 3,321  | 6  | 0.9 | I4, III 10    |
| 7 | 738    | 5  | 1.0 | II6           |

GREAT LAKES (Figure 10)

|   |        |    |     |          |
|---|--------|----|-----|----------|
| 1 | 21,964 | 7  | 0.6 | II5      |
| 2 | 4,913  | 5  | 0.6 | II6      |
| 3 | 2,312  | 7  | 0.6 | II5      |
| 4 | 8,381  | 7  | 0.6 | II5      |
| 5 | 12,427 | 7  | 0.6 | II5      |
| 6 | 4,913  | 6  | 0.6 | II5, II7 |
| 7 | 1,445  | 5  | 0.6 | II6      |
| 8 | 14,739 | 10 | 0.6 | I2       |
| 9 | 32,946 | 10 | 0.6 | II, I2   |

\* Rank adjusted to climatic differences, "-" indicates no sulphur production.

TABLE 5-6

CANADIAN COASTAL SULPHUR EMISSIONS $(10^6 \text{ gSy}^{-1})$ PACIFIC COAST (Figure 12)

|   |        |
|---|--------|
| 1 | 10,440 |
| 2 | 11     |
| 3 | 2      |
| 4 | 1      |
| 5 | 1      |
| 6 | 11     |

Total 10,470

ARCTIC COAST (Figure 13)

|    |     |
|----|-----|
| 1  | 10  |
| 2a | 72  |
| 2b | 1   |
| 11 | 1   |
| 12 | < 1 |

Total 84

ATLANTIC COAST (Figure 8 & 9)

|   |        |
|---|--------|
| 1 | < 1    |
| 2 | < 1    |
| 3 | 21,000 |
| 4 | 13,500 |
| 5 | 10     |
| 6 | 302    |
| 7 | 738    |

Total 35,550

GREAT LAKES (Figure 10)

|   |       |
|---|-------|
| 1 | 131   |
| 2 | 2,946 |
| 3 | 14    |
| 4 | 50    |
| 5 | 72    |
| 6 | 295   |
| 7 | 867   |
| 8 | < 1   |
| 9 | < 1   |

Total 4,375

CANADA - Total 50,500  
 $(.05 \text{ TgSy}^{-1})$



TABLE 5-7

ESTIMATED BIOGENIC SULPHUR PRODUCTION  
FROM FRESHWATER LAKES

| Province         | Lake Area<br>(10 <sup>9</sup> m <sup>2</sup> ) | Lake Type and Area | Rank | Sulphur Production<br>(10 <sup>6</sup> gS yr <sup>-1</sup> ) | Total Sulphur Production by Province<br>(10 <sup>6</sup> gS yr <sup>-1</sup> ) |
|------------------|------------------------------------------------|--------------------|------|--------------------------------------------------------------|--------------------------------------------------------------------------------|
| Newfoundland     | 34.0                                           | Eutrophic          | 4    | 6-7                                                          | 200                                                                            |
|                  |                                                | Other              | 30   | 9                                                            | 3                                                                              |
|                  |                                                |                    |      |                                                              | 203                                                                            |
| Nova Scotia      | 2.6                                            | Eutrophic          | 1.0  | 6                                                            | 100                                                                            |
|                  |                                                | Other              | 1.6  | 8                                                            | 2                                                                              |
|                  |                                                |                    |      |                                                              | 102                                                                            |
| New Brunswick    | 1.3                                            | Eutrophic          | 0.3  | 6                                                            | 30                                                                             |
|                  |                                                | Other              | 1.0  | 8                                                            | 1                                                                              |
|                  |                                                |                    |      |                                                              | 31                                                                             |
| Quebec           | 183.9                                          | Eutrophic          | 13   | 6                                                            | 1300                                                                           |
|                  |                                                | Other              | 171  | 8                                                            | 171                                                                            |
|                  |                                                |                    |      |                                                              | 1471                                                                           |
| Ontario          | 177.4                                          | Eutrophic          | 34   | 6                                                            | 3400                                                                           |
|                  |                                                | Other              | 143  | 8                                                            | 143                                                                            |
|                  |                                                |                    |      |                                                              | 3543                                                                           |
| Manitoba         | 101.6                                          | Eutrophic          | 52   | 6-7                                                          | 2600                                                                           |
|                  |                                                | Other              | 50   | 8                                                            | 50                                                                             |
|                  |                                                |                    |      |                                                              | 2650                                                                           |
| Saskatchewan     | 82.0                                           | Eutrophic          | 48   | 6-7                                                          | 2400                                                                           |
|                  |                                                | Other              | 34   | 8                                                            | 34                                                                             |
|                  |                                                |                    |      |                                                              | 2434                                                                           |
| Alberta          | 17.0                                           | Eutrophic          | 13   | 6-7                                                          | 650                                                                            |
|                  |                                                | Other              | 4    | 8                                                            | 4                                                                              |
|                  |                                                |                    |      |                                                              | 654                                                                            |
| British Columbia | 18.0                                           | Eutrophic          | 8    | 6                                                            | 800                                                                            |
|                  |                                                | Other              | 10   | 8                                                            | 10                                                                             |
|                  |                                                |                    |      |                                                              | 810                                                                            |
| Canada Total     |                                                |                    |      |                                                              | 11,898                                                                         |

Note: No estimate was made for freshwater lakes of the Territories

## 5.2 OTHER NATURAL EMISSIONS

This section presents the estimates of sulphur emissions from sea spray and lake spray (Tables 5-8 and 5-9). The estimated sea salt sulphate emissions are from the 320 kilometre fishing zone on the Pacific and Atlantic coasts, the entire areas of Hudson's Bay, and the area of Beaufort Sea south of the permanent ice pack. The annual sea and lake  $\text{SO}_4$  emissions were estimated from rates derived in Section 4.3.1. The annual emissions for forest fires has been previously presented in Table 4-4.



TABLE 5-8

## SULPHUR FROM SEA SALT SPRAY

|                | Area<br>(km <sup>2</sup> ) | Flux Rate<br>(10 <sup>6</sup> gS Km <sup>-2</sup> yr <sup>-1</sup> ) | Annual Sulphur<br>Emissions<br>(10 <sup>6</sup> gS) |
|----------------|----------------------------|----------------------------------------------------------------------|-----------------------------------------------------|
| Pacific Coast  | 390,000*                   | 0.07                                                                 | 27,300                                              |
| Atlantic Coast | 520,000*                   | 0.17                                                                 | 88,400                                              |
| Labrador Sea   | 320,000*                   | 0.04                                                                 | 12,800                                              |
| Hudson Bay     | 820,000                    | 0.07                                                                 | 57,400                                              |
| Beaufort Sea   | 50,000                     | 0.06                                                                 | 3,000                                               |
|                |                            | Total                                                                | 188,900                                             |

\* area of coastal waters to 320 km limit

TABLE 5-9  
LAKE SULPHATE EMISSIONS

| Lake                      | Area <sup>+</sup><br>(Km <sup>2</sup> ) | Ice-free<br>Period <sup>*</sup> | Annual<br>Sulphur<br>Emissions | Provincial<br>Emissions<br>(10 <sup>6</sup> gs yr <sup>-1</sup> ) |
|---------------------------|-----------------------------------------|---------------------------------|--------------------------------|-------------------------------------------------------------------|
| Newfoundland and Labrador |                                         |                                 |                                |                                                                   |
| Michikamn                 | 2031                                    | 0.2                             | 30                             |                                                                   |
| Smallwood Reservoir       | 6475                                    | 0.2                             | 90                             | 120                                                               |
| Quebec                    |                                         |                                 |                                |                                                                   |
| Bienville                 | 1248                                    | 0.5                             | 40                             |                                                                   |
| Ean Claire                | 1383                                    | 0.5                             | 50                             |                                                                   |
| Goain Reservoir           | 1570                                    | 0.5                             | 60                             |                                                                   |
| Mistassini                | 2336                                    | 0.5                             | 80                             |                                                                   |
| Saint-Jean                | 1002                                    | 0.5                             | 40                             | 270                                                               |
| Ontario                   |                                         |                                 |                                |                                                                   |
| Lake of Woods             | 3149                                    | 0.5                             | 110                            |                                                                   |
| Nipigon                   | 4848                                    | 0.5                             | 170                            |                                                                   |
| Seul                      | 1658                                    | 0.5                             | 60                             |                                                                   |
| Superior                  | 28749                                   | 0.6                             | 1210                           |                                                                   |
| Huron                     | 36001                                   | 0.6                             | 1510                           |                                                                   |
| Erie                      | 12769                                   | 0.6                             | 540                            |                                                                   |
| Ontario                   | 10049                                   | 0.6                             | 420                            | 4020                                                              |
| Manitoba                  |                                         |                                 |                                |                                                                   |
| Cedar                     | 1352                                    | 0.3                             | 30                             |                                                                   |
| Gods                      | 1150                                    | 0.3                             | 20                             |                                                                   |
| Island                    | 1222                                    | 0.3                             | 30                             |                                                                   |
| Manitoba                  | 4659                                    | 0.5                             | 100                            |                                                                   |
| Moose                     | 1368                                    | 0.3                             | 30                             |                                                                   |
| Southern Indian           | 2248                                    | 0.3                             | 50                             |                                                                   |
| Winnipeg                  | 24390                                   | 0.4                             | 680                            |                                                                   |
| Winnipegosis              | 5374                                    | 0.4                             | 150                            | 1090                                                              |



TABLE 5-9 (CONT'D)

## LAKE SULPHATE EMISSIONS

| Lake                  | Area<br>(Km <sup>2</sup> ) | Ice-free<br>Period | Annual<br>Sulphur<br>Emissions | Provincial<br>Emissions<br>(10 <sup>6</sup> gs yr <sup>-1</sup> ) |
|-----------------------|----------------------------|--------------------|--------------------------------|-------------------------------------------------------------------|
| Saskatchewan          |                            |                    |                                |                                                                   |
| Athabasca             | 7935                       | 0.2                | 110                            |                                                                   |
| Cree                  | 1435                       | 0.2                | 20                             |                                                                   |
| La Rouse              | 1414                       | 0.2                | 20                             |                                                                   |
| Reindeer              | 6651                       | 0.2                | 90                             |                                                                   |
| Wollaston             | 2681                       | 0.2                | 20                             | 260                                                               |
| Alberta               |                            |                    |                                |                                                                   |
| Claire                | 1437                       | 0.2                | 20                             |                                                                   |
| Lesser Slave          | 1168                       | 0.2                | 20                             | 40                                                                |
| British Columbia      |                            |                    |                                |                                                                   |
| Williston             | 1761                       | 0.4                | 50                             | 50                                                                |
| Northwest Territories |                            |                    |                                |                                                                   |
| Aberdeen              | 1101                       | 0.2                | 20                             |                                                                   |
| Amadjuak              | 3116                       | 0.2                | 40                             |                                                                   |
| Dubawnt               | 3833                       | 0.2                | 50                             |                                                                   |
| Great Bear            | 31328                      | 0.2                | 440                            |                                                                   |
| Great Slave           | 28570                      | 0.3                | 600                            |                                                                   |
| Kasba                 | 1342                       | 0.2                | 20                             |                                                                   |
| La Martre             | 1777                       | 0.2                | 20                             |                                                                   |
| Mackay                | 1062                       | 0.2                | 10                             |                                                                   |
| Netillins             | 5543                       | 0.2                | 80                             |                                                                   |
| Nueltin               | 2279                       | 0.2                | 30                             |                                                                   |
| Takiguak              | 1080                       | 0.2                | 10                             |                                                                   |
| Yathkyed              | 1448                       | 0.2                | 20                             | 1340                                                              |
| Canada Total          |                            |                    |                                | 7190                                                              |

<sup>†</sup> Lake areas from Statistics Canada 1977  
Special Canada Year Book 1976-77

<sup>\*</sup> Ice-free periods from Environment  
Canada, Atmospheric Environment Service  
Ice Thickness Data for Selected Stations,  
1971-72





## 6. DATA GAPS AND UNCERTAINTIES

The investigation of natural emissions of sulphur has only recently gained momentum. As a consequence, only preliminary data, if any, are available which are useful in quantifying emission rates of natural compounds. In addition, the velocity of the prominent measurement techniques currently used is being re-evaluated.

Global sulphur budgets, with their inherent weakness of using backfitting estimates to balance the sulphur cycle, do not provide accurate data for determining natural emissions on a regional basis. These budgets also cannot account for regional differences in sulphur production which vary with factors such as soil climates, growing seasons, ice cover, and prevalence of water bodies. Similarly, applying spot measurements of flux rates (which in themselves may not be accurate) to large scale integrated features of soils and hydrology leads to inaccuracies which are significant.

The estimates in this report, out of necessity, were generated using the latter approach, modified by a semi-quantitative interpretation of the more productive generation mechanisms.

The biogenic natural sulphur emissions estimated for Canada are about  $0.3 \text{ TgSyr}^{-1}$  compared to a value of about  $5 \text{ TgSyr}^{-1}$  reported by Katz (1977). This latter value was derived by proportioning the estimated budget of the northern hemisphere (by Kellogg et.al. 1972) with the ratio of Canadian land area to hemispheric land area.

This approach does not take into account the extreme variability of climatic, terrestrial, and hydrographic conditions in the hemisphere. Most evidence indicates a higher production of sulphur by biogenic sources in equatorial areas. Biogenic flux rates have been shown to increase by two orders of magnitude as the temperature increases from 5 - 10°C to 30°C (Adams 1978a, Georgii 1978). The latter temperature is typical of equatorial regions while the first value is typical of a large proportion of Canada. If this temperature factor is considered, it appears that Katz' (1977) estimate is too high, possibly by an order of magnitude.

The approach in this study has used average soils and marine conditions on a scale of about 200 km<sup>2</sup> and a logarithmic ranking of sulphur productivity. Contributions by high production areas of smaller size may consequently be underestimated. The range of variation in the present estimate of 0.3 TgSyr<sup>-1</sup> could be within plus or minus an order of magnitude (i.e. 0.03-3). However, the limitations of the approach of Katz (1977) and the possible underestimations in this study indicate that the total biogenic sulphur emissions in Canada range from 0.3 to 1.0 TgSyr<sup>-1</sup>.

The validity of current measurement and analytic techniques must be ascertained before a more accurate estimate is made of biogenic sulphur emissions. A U.S. National Science Foundation workshop on the chemistry of the troposphere, held in the fall of 1978, concluded that none of the presently available techniques used to estimate biogenic sulphur emissions are reliable (D.R. Hitchcock, pers. comm.).

The chamber method used by various researchers in the field appears to inhibit H<sub>2</sub>S emissions much more than emissions of organic sulphur compounds. In addition, this technique may



also disturb sediment - and soil - air interfaces. Biogenic  $H_2S$  only escapes to the air when the anaerobic producing media is close to the atmospheric boundary layer. If an overlying aerobic layer is disturbed by an insitu measurement device, erroneously high levels of biogenic sulphides may be detected in the air above the interface.

Vertical mean profiles of natural sulphur concentration data are commonly used to calculate the flux of a sulphur compound into the atmosphere. This gradient technique assumes that the horizontal extent of the emitting source is large compared with the measuring altitude and that there are no temporal variations in the emission rate. This is rarely or never achieved -  $H_2S$  production has been shown to be extremely variable in both space and time.

The relative contributions of gaseous compounds other than  $H_2S$  to total sulphur flux rates for biogenic sources has only been examined by Adams (1978a). This is a serious data gap since there is no other available comparison to obtain an indication of flux rate variability. Consequently the emissions from biogenic sources estimated from soils and marine areas are only representative of the evolution of  $H_2S$ .

What information is available indicates that the volatile organic sulphur compounds evolved from a variety of soils are at relatively constant levels. Such emissions appear to be a general feature of soils. It appears at this time that sulphur emission variability is attributable mainly to hydrogen sulphide. Emission of other compounds in various soil types represents a more uniform background level. While hydrogen sulphide may be produced in apparently aerobic soils, much larger production occurs in waterlogged and reducing soils.

The behaviour of methylating and related bacteria involved in the production of DMS, methylmercaptan and related compounds is poorly understood, so that relationship between soil sulphur production and soil condition in other than anaerobic soils is at present unknown.

Release rates of DMS (Lovelock et al. 1972) from vegetation were used in estimating a sulphur production from vegetation in this study. Other organic sulphur compounds, potentially produced by plants, were not accounted for in this study due to lack of information. Also, there are no data available on the mechanism for production of volatile sulphur compounds from living and senescent plants, although production during enzymic breakdown of protein material is possible.



## 7. REFERENCES

- Adams, D.F., S.O. Farwell, M.R. Pack, W.L. Bamesberger, and A.E. Sherrard, 1978a. Measurement of biogenic sulphur-containing gas emissions from soils and vegetation. Preprint 1978, Annual Meeting of Air Pollution Control Association, Houston, Texas.
- Adams, D.F., S.O. Farwell, M.R. Pack, and W. L. Bamesberger, 1978b. Preliminary measurements of biogenic sulphur-containing gas emissions from soils. To be published in Journal of Air Pollution Control Association.
- Adams, D.F., S.O. Farwell, M.R. Pack, and E. Robinson, 1978c. An initial emission inventory of biogenic sulphur flux from terrestrial surfaces. Paper presented at Annual Meeting of PNWIS/APCA, Portland, Oregon, November 8-10, 1978.
- Agriculture Canada, 1977. Soils of Canada. Vol. 1 Soil Report and Vol. 2 Inventory. Supply and Services, Ottawa, Canada.
- Axelrod, H.D., J.H. Cary, J.E. Bonelli, and J.P. Lodge Jr., 1969. Fluorescence determination of sub-parts per billion hydrogen sulphide in the atmosphere - Analyt. Chem. 41:1856-1858.
- Banwart, W.L., and J.M. Bremner, 1975. Evolution of volatile sulphur compounds from soils treated with sulphur-containing organic materials. Soil. Biol. Biochem 8:436.
- Berry, R.L., 1979. The Canadian network for sampling precipitation (CANSAP) project. Summary for the period May 1977 to April 1978. LRTRAP 79-1. Air Quality and Inter-Environmental Research Branch, Atmospheric Environment Service, Downsview, Ontario.
- Brannon, J.M., 1973. Seasonal variation of nutrients and physiochemical properties in the salt marsh soils of Barataria Bay, Louisiana. Masters Thesis. Louisiana State University. Baton Rouge, Louisiana.
- Breeding, R.J., J.P. Lodge Jr., J.B. Pate, D.C. Sheesly, H.B. Klonis, B.T. Fogle, J.A. Anderson, T.R. Englert, P.L. Haagenson, R.B. McBeth, A.L. Morris, R. Pouge, and A.F. Wartburg, 1973. Background trace gas concentrations in the central United States. J. Geophys. Res. 79:7057-7064.



- Burgeff, H., 1961. Mikrobiologie des Hochmoores; mit besonderer Berücksichtigung der Erikazeen-Pilzsymbiose. G. Fischer, Stuttgart. 197 pp.
- Butcher, S.S., and R.J. Charlson, 1972. An Introduction to Air Chemistry, New York: Academic Press, 241 pp.
- Cadle, R.D. and M. Ledford, 1966. The reaction of ozone with hydrogen sulfide. Int. J. Air. Water. Pollut. 10:25-30.
- Cadle, R.D., 1973. Particulate matter in the lower atmosphere. In: Chemistry of the Lower Atmosphere. S.I. Rasool, ed. Plenum Press, New York, 335 pp.
- Castenholz, R.W., 1969. Thermophilic blue-green algae and the thermal environment. Bact. Reviews. 33:476-504.
- Canada Dept. of Transport, 1968. Climatic Normals, Vol. 5 Wind. Meteorological Branch, Toronto, Ontario.
- Castleman, A.W. Jr., H.R. Munkelwitz, and B. Manowitz, 1974. Isotopic studies of the sulphur component of the stratospheric aerosol layer. Tellus 26:222-234.
- Challenger, F., 1951: Biological methylations. In: Advances in Enzymology, F.F. Nord, ed. Vol. 12.
- Chung, Y.S., 1978. The distribution of atmospheric sulphates in Canada and its relationship to long-range transport of air pollutants. Atmos. Env., 12:1471-1480.
- Connell, W.E. and W.H. Patrick, 1968. Sulphate reduction in soil: effects of redox potential and pH. Science 159:86-87.
- Conway, E.J., 1942. The chemical evolution of the ocean. Proc. R. Ir. Acad. 48:161-212.
- Conway, E.J., 1943. Mean geochemical data in relation to oceanic evolution. Proc. R. Ir. Acad. A48:119-159.
- Cox, R.A. and F.J. Sandalls, 1974. The photo-oxidation of hydrogen sulphide and dimethyl sulphide in air. Atmos. Env. 8:1269-1281.
- Cox, R.A., 1975. Atmospheric photo-oxidation reactions. U.K.A.E.A. Report AERE-R 8132.
- Drozдова, U.M., O.P. Petrenchuk, E.S. Selezneva, and D.F. Svistov, 1964. The Chemical Composition of Atmospheric Precipitation over European Territory of the U.S.S.R. Leningrad: Gidrometeorologitsheskoe Izd. 209 pp.



- Durbin, W.G., and G.D. White, 1961. Measurement of the vertical distribution of atmospheric chloride particles. *Tellus* 13: 200-273.
- Engler, R.M. and W.H. Patrick, 1973. Sulfate reduction and sulfide oxidation in flooded soil as affected by chemical oxidants. *Soil Sci. Soc. Amer. Proc.* 37:685-688.
- Engler, R.M., and W.H. Patrick, 1975. Stability of sulfides of manganese, iron, zinc, copper and mercury in flooded and nonflooded soil. *Soil Science* 119:217-221.
- Environment Canada, 1972. Ice thickness data for selected stations 1971-72. Atmospheric Environment Service, Downsview, Ontario.
- Eriksson, E. 1963. The yearly circulation of sulphur in nature. *J. Geophys. Res.* 68:4001-4008.
- Evans, C.C., and S.E. Allen, 1971. Nutrient losses in smoke produced during heather burning. *Oikos* 22:149-154.
- Friend, J.P. 1973. The global sulfur cycle. In: *Chemistry of the Lower Atmosphere*. S.I. Rasool, ed. Plenum Press, New York, 335 pp.
- Faller, N., 1971. Effects of atmospheric SO<sub>2</sub> on plants. *The Sulphur Institute Journal*, Winter 1970-71; 5-7.
- Geological Survey of Canada, 1970. *Geology and economic minerals of Canada*. R.J.W. Douglas, ed. Dept. of Energy, Mines and Resources, Ottawa.
- Georgii, H.W., H. Clanele, W. Jaeschke, and Malewski, 1976. Messauger von H<sub>2</sub>S in Bodennähe und derunteren troposphäre. In: *Arbeitsbericht des SFB 73 Atmosphärische Spurentoffe: Frankfurt a.m-Mainz*.
- Georgii, H.W., 1978. Large scale spatial and temporal distribution of sulphur compounds. *Atmos. Envir.* 12: 681-690.
- Gillette, D.A. and I.H. Bifford Jr., 1971. Composition of tropospheric aerosols as a function of altitude. *J. Atmos. Sci.* 28:1199
- Granat, L. 1976. A global atmospheric sulphur budget. In: *Nitrogen, Phosphorus and Sulphur Global Cycles*, SCOPE Report 7. *Eco. Bull.* (Stockholm) 22.
- Gravenhorst, G. and U. Jendrieke, 1974. Konzentrationen verhältnisse chemischer Komponenteuten des aerosols über dem nord-Atlantik. *"Meteor" Forsch-Ergebn.* B,9:68-77.
- Gravenhorst, G. 1974. The sulphate component in aerosol samples over the north Atlantic. *"Meteor" Forsch-Ergebn.* B,10:22-31.



- Gravenhorst, G., 1978. Maritime sulfate over the north Atlantic. *Atmos. Envir.* 12:707-713.
- Hallberg, R.O., 1976. A global sulphur cycle based on a preindustrial steady state of the pedosphere. In: Nitrogen, Phosphorus and Sulphur-Global Cycles. SCOPE Report 7. *Ecol. Bull.* 22.
- Hales, J.M., J.O. Wilkes and J.L. York, 1974. Some recent measurements of H<sub>2</sub>S oxidation rates and their applications in atmospheric chemistry. *Tellus* 26:277-283.
- Hansen, M.H., K. Ingvorsen, and B.B. Jorgenson, 1978. Mechanisms of hydrogen sulfide release from coastal marine sediments to the atmosphere. *Limnol. Oceanogr.* 23:68-76.
- Hanst, P.L. L.L. Spiller, D.M. Watts, J.W. Spence and M.F. Miller, 1975. Infrared measurements of fluorocarbons, carbon tetrachloride, carbonyl sulfide and other atmospheric trace gases. *J. Air Poll. Contr. Assoc.* 12:1220-1226.
- Harter, R.D. and E.O. McLean, 1965. The effect of moisture level and incubation time on the chemical equilibria of a Toledo clay loam soil. *Agron. J.* 57:583-588.
- Hennick, B., 1971. The role of hydrogen sulfide in the ecology of Calamagrostis canadensis and Glyceria striata. M.Sc. Thesis. Univ. Toronto. May 1971.
- Hitchcock, D.R., and E.A. Wechsler, 1972. Biological cycling of atmospheric trace gases. Final report prepared for National Aeronautics and Space Administration, Washington, D.C.
- Hitchcock, D.R., 1975. Dimethyl sulfide emissions to the global atmosphere. *Chemosphere* 4:137-138.
- Hitchcock, D.R., 1976. Microbiological contributions to the atmospheric load of particulate sulfate. In: Environmental Biogeochemistry, J.O. Nriagu, ed. Ann Arbor Sci.
- Hitchcock, D.R., 1977. Biogenic sulfur sources and air quality in the United States. Final Report Prepared for National Science Foundation, Washington, D.C., NTIS PB-273 824.
- Hitchcock, D.R., L.L. Spiller, and W.E. Wilson, 1978. Biogenic sulfur compounds in coastal atmospheres of North Carolina. U.S. Environmental Protection Agency, EPA-600/3-78-061, Research Triangle park, North Carolina.



- Hosler, W.T. and I.R. Kaplan, 1966. Isotope geochemistry of sedimentary sulphates. Chem. Geol. 1:93-135.
- Jaeschke, W. and W. Hanold., 1977. New methods and first results of measuring atmospheric H<sub>2</sub>S and SO<sub>2</sub> in the ppb range. WMO special Env. Rept. No. 10:193-198.
- Jaeschke, W., 1978. New methods for the analysis of SO<sub>2</sub> and H<sub>2</sub>S in remote areas and their application to the atmosphere. Atmos. Envir. 12:715-721.
- Jaeschke, W., H.W. Georgii, H. Claude, and H. Malewski, 1978. Contributions of H<sub>2</sub>S to the atmospheric sulphur cycle. Pageoph 116:465-475.
- Jensen, M.L. ed., 1962. Biogeochemistry of sulfur isotopes. Proceedings of a National Science Foundation Conference. Yale University.
- Jorgensen, B.B., 1977a. Bacterial sulfate reduction within reduced microuiches of oxidized marine sediments. Mar. Biol. 41: 7-17.
- Jorgensen, B.B., 1977b. Distributions of colourless sulfur bacteria (*Beggiatoa* spp.) in a coastal marine sediment. Mar. Biol. 41:19-28.
- Junge, C.E., 1963. Atmospheric Chemistry and Radioactivity. Academic Press, New York.
- Katz, M., 1977. The Canadian sulphur problem. Chpt.1 in: Sulphur and its inorganic deriviatives in the Canadian environment. National Research Council of Canada, NRCC No. 2155, Ottawa, Canada.
- Kellogg, W.W., R.O. Cadle, E.R. Allen, A.C. Lazrus, and E.A. Martell, 1972. The sulphur cycle. Science 175:587-
- Liss, P.S., and P.G. Slater, 1974. Fluxes of gases across the air-sea interface. Nature 247:181-185.
- Lodge, J.P. Jr., 1955. J. Met. 12, 493
- Lodge, J.P. Jr., and J.B. Pate, 1966. Atmospheric gases and particulates in Panama. Science 153:408-410.
- Lodge, J.P. Jr., P.A. Machado, J.B. Pate, D.C. Sheesley, and A.F. Wartburg, 1974. Atmospheric trace chemistry in the American humid tropics. Tellus 26:250-253.
- Lovelock, J.E., R.J. Maggs, and R.A. Rasmussen, 1972. Atmospheric dimethyl sulfide and the natural sulphur cycle. Nature 237:452-453.



- .. Lovelock, J.E., 1974. CS<sub>2</sub> and the natural sulphur cycle. Nature 248:625-626.
- Lovett, R.F., 1978. Quantitative measurement of airborne sea-salt in the North Atlantic. Tellus 30:358-364.
- Maroulis, P.J., and A.R. Bandy, 1977. Estimate of the contribution of biologically produced dimethyl sulfide to the global sulfur cycle. Science 196:647-648.
- Martin, A. and F.R. Barber, 1978. Some observations of acidity and sulphur in rainwater from rural sites in central England and Wales. Atmos. Envir. 12: 1481-1487.
- Meszaros, A., and K. Vissy, 1974. Concentration, size distribution and chemical nature of atmospheric aerosol particles in remote oceanic areas. J. Aerosol Sci. 5: 101-110.
- Meszaros, E., 1978. Concentration of sulfur compounds in remote continental and maritime areas. Atmos. Envir. 12:699-705.
- Natusch, D., H. Klonis, H. Axelrod, R. Teck, and J. Lodge, 1972. Sensitive method for the measurement of atmospheric hydrogen sulfide. Anal. Chem. 44:2067-2070.
- Naughton, J.J., E.F. Heald, and I.L. Barnes Jr. J. Geophys. Res. 68:539-.
- Nguyen, B.C., B. Bonsang, and G. Lambert, 1974. The atmospheric concentration of sulphur dioxide and sulphate aerosols over Antarctic, subantarctic areas and oceans. Tellus 26: 241-249.
- Nochumson, D. 1979. Comment on "Gaseous sulfur pollutants from urban and natural sources." J. Air Poll. Cont. Assoc. 29: 164-165.
- Nriagu, J.O. 1975. Sulphur isotopic variations in relation to sulphur pollution of Lake Erie. In: Isotope ratios as pollutant source and behaviour indicators. International Atomic Energy Agency, Vienna.
- Nriagu, J.O. & Coker, R.D. 1978. Isotopic composition of sulfur in precipitation within the Great Lakes Basin. Tellus 30: 365-375.
- Owens, E.H. 1977. Coastal Environments of Canada. The Impact and Cleanup of Oil Spills. Environmental Protection Service Report EPS-3-EC-77-13. Ottawa, Ontario.

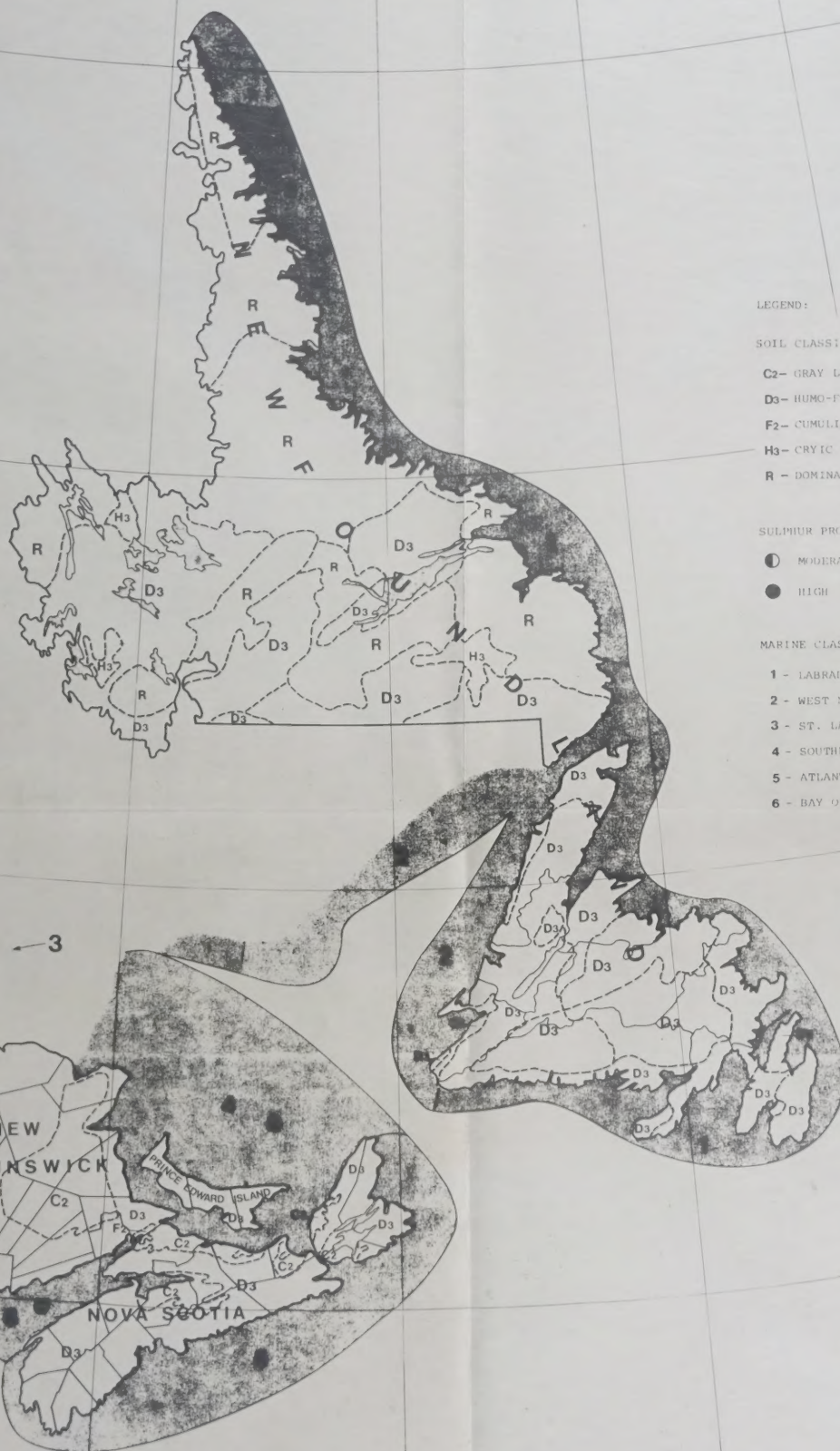


- Pearsall, W.H. and E. Gorham, 1956. Production ecology. *Oikos* 7: 193-201.
- Penkett, S.A. 1972. Oxidation of  $\text{SO}_2$  and other atmospheric gases by ozone in aqueous solution. *Nature* 240: 252-256.
- Prahm, L.P., U.P. Torp, and R.M. Stern, 1975. Deposition and transformation rates of sulfur oxides during atmospheric transport over the Atlantic. Rep. Copenhagen: Danish Meteorological Instit., 61 pp.
- Rasmussen, R.A. 1974. Emission of biogenic hydrogen sulfide. *Tellus* 26: 254-260.
- Rennie, P.J. 1972. unpublished data. cited in NRC Report Sulphur and its Inorganic Derivatives in the Canadian Environment.
- Rennie, P.J. and R.L. Halstead, 1977. The effects of sulphur on plants in Canada. In: Sulphur and its Inorganic Derivatives in the Canadian Environment. National Research Council NRCC No. 15015, Ottawa, Canada.
- Robinson, E. and R.C. Robbins, 1968. Sources, abundance, and fate of gaseous atmospheric pollutants. Final Report SRI Project PR-6755, Stanford Research Inst., Menlo Park, California.
- Robinson, E. and R.C. Robbins, 1970. Gaseous sulfur pollutants from urban and natural sources. *J. Air Poll. Cont. Assoc.* 20: 233- .
- Sandalls, F.J., and S.A. Penkett, 1977. Measurements of carbon disulphide in the atmosphere. *Atmos. Envir.* 11: 197-199.
- Selezneva, E.S., O.P. Pentrenchuk, and P.E. Svistov, 1967... On the investigation of distribution and chemical composition of natural aerosols over different regions of the USSR - Symposium on Tropospheric Aerosols and Radioactive Tracers, Leningrad: IUCC.
- Siman, G., and S.L. Jansson, 1976a. Sulphur exchange between soil and atmosphere with special attention to sulphur release directly to the atmosphere 1. Formation of gaseous sulphur compounds in the soil. *Swedish J. Agric. Res* 6: 37-45.
- Siman, G. and S.L. Jansson, 1976b. Sulphur exchange between soil and atmosphere with special attention to sulphur release directly to the atmosphere 2. The role of vegetation in sulphur exchange between soil and atmosphere. *Swedish J. Agric. Res.* 6: 135-144.



- Slatt, B.J., D.F. Natusch, J.M. Prospero, and D.L. Savoie, 1978. Hydrogen sulfide in the atmosphere of the northern equatorial Atlantic ocean and its relation to the global sulfur cycle. *Atmos. Envir.* 12: 981-991.
- Sparling, J.H. and B.M. Hennick, 1974. The production of hydrogen sulphide in peat. *Folia Microbiol.* 19: 59-66.
- Statistics Canada, 1977. *Canada Year Book* 1976-77.
- Stuhl, F. 1974. Determination of the rate constant for the reaction OH and H<sub>2</sub>S by a pulsed photolysis - resonance fluorescence method. *Ber. d. Bunsen Ges.* 78: 230-232.
- Sverdrup, H.U., M.W. Johnson, and R.H. Fleming, 1949. *The Oceans, their Physics, Chemistry, and General Biology.* Prentice-Hall, Englewood Cliffs, N.J.
- Takai, Y. and T. Kamura, 1966. *Folia Microbiol.* 11: 304.
- Toba V. 1965. On the giant sea-salt particles in the atmosphere 1. General features of the distribution. *Tellus* 17: 131-145.
- U.S. Environmental Protection Agency. 1976. *Compilation of Air Pollutant Emission Factors. Second Edition Part B. AP-42.* Research Triangle Park, N.C.
- U.S. Geological Survey. 1965. Thermal springs of the United States and other countries of the world - a summary. *Professional Paper* 492.
- Vamos, R., 1964. Release of hydrogen sulphide from muds. *J. Soil Sci.* 15: 103-109.
- Vines, R.G., L. Gibson, A.B. Hatch, N.K. King, D.A. MacArthur, D.R. Packham, and R.J. Taylor, 1971. The nature, properties and behaviour of bush-fire smokes. C.S.I.R.O., Australia. *Div. Appl. Chem., Tech. Paper* 1: 32 pp.
- Westlake, D.F., 1963. Comparisons of plant productivity. *Biol. Rev.* 38: 385-425.
- Whittaker, R.H., 1970. *Communities and Ecosystems.* MacMillan Press, New York.
- Woodcock, A.H., 1953. Salt nuclei in marine air as a function of altitutte and windforce. *J. Meteorol.* 10: 362-371.
- Woodcock, A.H., 1957. Atmospheric sea-salt nuclei data for Project Shower. *Tellus* 9: 521-527.





#### LEGEND:

#### SOIL CLASSIFICATION

- C2- GRAY LUVISOL
- D3- HUMO-FERRIC PODZOL
- F2- CUMULIC REGOSOL
- H3- CRYIC FIBROSOL
- R - DOMINANTLY ROCKLAND

#### SULPHUR PRODUCTION

- MODERATE
- HIGH

#### MARINE CLASSIFICATION

- 1 - LABRADOR; OUTER NEWFOUNDLAND
- 2 - WEST NEWFOUNDLAND; NORTHERN GULF
- 3 - ST. LAWRENCE ESTUARY
- 4 - SOUTHERN GULF OF ST. LAWRENCE
- 5 - ATLANTIC NOVA SCOTIA
- 6 - BAY OF FUNDY

FIGURE 8

SOIL AND MARINE CLASSIFICATIONS  
MARITIME PROVINCES







